Measuring Asphaltenes and Resins, and Dipole Moment in Petroleum Fluids

Lamia Goual
Earth Science and Engineering, Imperial College, London SW7 2BP, UK

Abbas Firoozabadi
Reservoir Engineering Research Institute, Palo Alto, CA 94306

A petroleum fluid can be divided into three types of species: asphaltenes, resins, and oils. Asphaltenes and resins are polar, while the rest of the so-called oils are either nonpolar or mildly polar. The interaction among these species strongly affect asphaltene precipitation from petroleum fluids. Different measuring methods for asphaltenes in a petroleum fluid give similar results, but different results for the resin content of a petroleum fluid. In addition to the amount affecting precipitation, the polarity of asphaltenes and resins affects precipitation strongly. The Onsager formulation of dipolar moments was used to measure the dipole moment of asphaltenes, resins and the oil species from eight different petroleum fluids from various parts of the world. The dipole moment, a measure of polarity, for resins was measured in this work for the first time. Results showed that resin separated from a petroleum fluid by propane is part of the total resin. Adsorption methods, however, give the total amount of resins. For a given petroleum fluid, asphaltenes had a higher dipole moment than resins. However, resins from one petroleum fluid can have a higher dipole moment than asphaltenes from another petroleum fluid.

Introduction

A large number of subsurface petroleum reservoirs from various parts of the world experience asphaltene precipitation in the subsurface formation, in the wellbore, in the well, and in the surface facilities and pipelines. Asphaltene precipitation is undesirable because it reduces well productivity and limits fluid flow. In some cases, asphaltene precipitation can result in complete plugging of flow lines. Paradoxically, the asphaltene precipitation is often observed in petroleum fluids that contain very low asphaltene content. A heavy petroleum fluid with an asphaltene content of say 20 wt % may not have precipitation problems. On the other hand, a light petroleum fluid with an asphaltene content of less than 0.2 wt % may precipitate asphaltene. Examples are the light petroleum fluid from the Hassi-Messaoud field in Algeria (44 API gravity) with an asphaltene content of 0.1 wt % that precipitates a considerable amount of deposit in tubings and surface facilities (Leontaritis and Mansoori, 1988). On the other hand, the heavy crude from Boscan in Venezuela (10 API gravity) containing approximately 17 wt % asphaltenes does not encounter asphaltene deposition (Leontaritis and Mansoori, 1988).

A petroleum fluid at atmospheric pressure and ambient temperature has three main constituents: (1) oils (that is, saturates and aromatics), (2) resins, and (3) asphaltenes. Oils are often nonpolar or are mildly polar (as we will see in this work). Asphaltenes and resins are polar and may associate to form micelles. In a petroleum fluid, asphaltenes and resins exist in the form of monomers, as well as in micelles (Pfeiffer and Saal, 1940; Swanson, 1942). In a micelle, the micellar core is formed from the self-association of asphaltene molecules, and resins adsorb onto the core surface to form the shell that also contains the oils (Firoozabadi, 1999). The properties and the amount of asphaltenes and resins affect the formation of micelles. One purpose of this work is to measure the properties that are believed to influence the micellar formation and precipitation. Another main objective is to find how to measure the amount of resins in a petroleum

---

Correspondence concerning this article should be addressed to A. Firoozabadi.

fluid. A petroleum fluid is a continuum of several thousands of molecules, and it is very difficult to define a cutoff between the asphaltene, the resin, and the oil fractions. Nevertheless, asphaltene molecules are believed to contain one or two aromatic chromophores (containing on average seven rings) with short aliphatic side-chains (Groenzin and Mullins, 2000). Resin molecules have a similar structure but smaller chromophores and relatively longer aliphatic side-chains, which increase their solubility in aliphatic solvents (Speight, 1999; Firoozabadi, 1999).

There is a wide range of methods for the measurement of the amount of asphaltenes and resins in petroleum fluids. The diversity of the methods is related to the operational definition of these fractions. Indeed, asphaltenes are defined as those hydrocarbons insoluble in an excess of *n*-pentane (or *n*-heptane). Resins remain soluble when petroleum fluid is mixed with *n*-pentane (or *n*-heptane) but can adsorb on surface-active materials such as fuller's earths, attapulgus clay, alumina, or silica gel (Speight, 1999). In addition, resins are insoluble in an excess of liquid propane, butane(s), and some other chemicals (such as acids, acetates, alcohols). Both asphaltenes and resins are represented by average properties such as average molecular weight and average dipole moment. In recent years, it has been demonstrated that the average molecular weight of asphaltenes and resins is less than 1,000 g/mol (Lian et al., 1994; Storm and Sheu, 1995; Groenzin and Mullins, 2000). There has been very little work on the measurement of asphaltenes and resins' dipole moment, despite their polar character. To the best of our knowledge, the dipole moment of resins has not yet been reported in the literature. The dipole moment depends on the structure and size of the molecule, and is a guide to the polarity generated by functional groups and metallic elements. The polarity of asphaltenes has often been related to heteroatom or metal content (Nalwaya et al., 1999; Kaminski et al., 1999). Swanson (1942) studied qualitatively the polarity of asphaltenes, resins, and oils by dielectric constant measurements in benzene solution at different frequencies. Asphaltenes were found to be highly polar while resins had intermediate polarity between asphaltenes and oils. Conversely, Ese et al. (1998) analyzed the adsorptive properties of asphaltenes and resins and concluded that resins were more polar than asphaltenes. Maruska and Rao (1987) investigated the dipole moment of asphaltenes and reported a value of 5.3 D (the symbol for debye) for a vacuum residue of a heavy crude. They used the Onsager theory (1936) to correlate the dipole moment of asphaltenes to the dielectric constant and refractive index. Because asphaltenes are solid, it was not possible to determine directly the dielectric constant by dielectric spectroscopy; instead, Maruska and Rao dissolved asphaltenes in dilute toluene solutions. At low asphaltene concentrations (<10 wt %), the dielectric constant and refractive index were found to vary linearly with concentration. The linear variations were then extrapolated to 100 wt % concentration to estimate the properties of pure asphaltenes. Halvorsen (1997) measured the dipole moment of asphaltenes from several North Sea crudes precipitated by *n*-pentane. Dielectric constants were determined by dielectric spectroscopy (100 Hz to 15 MHz), and a loop system allowed the circulation of *p*-xylene solutions from the dielectric cell to the impedance meter. Halvorsen used the Debye theory (1929) to relate the dielectric constant to the dipole moment of asphaltenes and reported values ranging from 4 to 17 D. In this work, it will be demonstrated that the Debye theory may not provide reliable results. A study of the dielectric behavior of hydrocarbon mixtures by Sen et al. (1992) revealed that the Debye theory can be used for mixtures of nonpolar liquids (such as *n*-octane in *n*-hexane), while the Onsager theory can be used for mixtures of polar and nonpolar liquids (such as acetone in *n*-hexane).

The standard procedures for asphaltene measurement are similar and generate comparable results. The methods consist mainly of precipitation by *n*-alkanes (*n*-pentane or *n*-heptane). Although acids and heavy paraffins may coprecipitate with asphaltenes (Becker, 2000; Newberry and Barker, 2000), precipitation with *n*-alkanes is the main separation method of asphaltenes from petroleum fluids. In Institute of Petroleum Standard IP 143 (1957), asphaltenes are separated from petroleum fluids with *n*-heptane; the precipitated phase is then washed for one hour with a reflux of hot heptane to remove waxy constituents. In the ASTM D-3279 method (1978), asphaltenes from petroleum residues are precipitated with *n*-heptane and filtered after 30 min of heating and stirring with a reflux system. In the ASTM D-893 method (1980), asphaltenes are precipitated from lubricating oils by centrifugation in *n*-heptane. Finally, in the Syncrude analytical method (1979), crudes are mixed with benzene prior to asphaltene precipitation with *n*-pentane. After 2-h settling in the dark, they are filtered and washed.

There are two main methods for separation of resins from petroleum fluids: (1) precipitation, and (2) adsorption. The precipitation by liquid propane is inspired from refinery processes and has found application in the laboratory by Schwager and Yen (1978), Murzakov et al. (1981), and others. Other precipitation methods using chemicals have also been proposed. In the standard ASTM D-2006 procedure (1970), resins are separated from rubber extender and processing oils by precipitation in sulfuric acid. A method prevalent in Germany applied by the German Petroleum Institute advocates the precipitation of asphalt (that is, asphaltenes and resins) from petroleum fluids with ethyl acetate and solubilization of resins from the precipitate with *n*-pentane (Andersen and Speight, 2001). The adsorption methods have been extensively used and consist of adsorbing resins on surface-active materials. The oils are eluted (that is, washed away from the column) with a nonpolar solvent, and the resins remain on the adsorbent until desorbed by a polar solvent. Following this separation scheme, a series of standard procedures have been established. The Syncrude analytical method (1979) separates resins by adsorption on attapulgus clay; oils are eluted with *n*-pentane and resins are desorbed by successive elution with methyl-ethyl-ketone and tetrahydrofuran/water (95/5 vol/vol). ASTM D-2007 (1991a) uses the same adsorbent and eluting solvent for oils, but a mixture of toluene and acetone (50/50 vol/vol) to desorb resins. In ASTM D-4124 (1991b), resins are adsorbed on activated alumina, and oils are eluted with *n*-heptane and toluene (33/67 vol/vol); a mixture of toluene–methanol–trichloroethylene (17/17/66 vol/vol/vol) recovers resins. In all the preceding methods, oils are eluted by the *n*-alkane used to precipitate asphaltenes. The separation is time-consuming and it is sometimes found that heavy aromatics are eluted with resins due to a high retention time in the column. This has oriented some to introduce a certain amount of aromatic solvent with n-alkanes to elute the oils. Callen et al. (1976) used 6 vol % dichloromethane in n-hexane, Farcasiu (1979) used 15 vol % toluene in n-heptane, Moinelo et al. (1988) used 36 vol % benzene in n-hexane, and more recently, McLean and Kilpatrick (1997) used 32 vol % toluene in n-heptane.

Resins recovered by precipitation or adsorption show marked differences in the amount and chemical composition. Even within adsorption methods, discrepancies can be found if adsorbents are different or elution time is varied (Wallace et al., 1987). Currently, resins are defined according to the solvents used for their separation. Considerable effort has been dedicated to the selection of appropriate polar solvents to desorb resins from surface-active materials, with less effort to the choice of nonpolar solvents to elute oils. The principle of resin separation by adsorption assumes that the nonpolar solvent should not dissolve any resin. Yet, aromatic solvents such as toluene or benzene are very good solvents for resins and their use may cause unreliablity for resin separation.

In this work, resins are separated by both precipitation and adsorption. In the adsorption method, different n-C_5/toluene volume ratios are used to recover oils in order to accelerate the separation and to ensure that heavy aromatics are washed from the column with oils. Because toluene can elute some resin constituents with oils, we would study the n-C_5/toluene volume ratio that separates oils by preserving all the constituents of resins in the resin fraction. This is possible by measuring the dipole moment of resins recovered in each test.

With the preceding background, the main objectives of this work are: (1) to devise a simple method for proper measurement and separation of resins in crudes, and (2) to determine the dipole moment of asphaltenes and resins. In the first part, we measure the resin content using a precipitation method with liquid propane and an adsorption method according to the modified ASTM D-2007 (1991a) procedure with different mixtures of n-pentane/toluene to elute the oils. Simplicity, scale, and practicality are considered when choosing the methods. In the second part, the theory of dipole moment is briefly reviewed and various methods are compared using chemicals with a known dipole moment. The appropriate method is selected and applied for measuring the dipole moment of asphaltenes and resins. The determination of asphaltene and resin dipole moments is important in that it allows the selection of a definitive procedure for resin measurement in crudes and provides a valuable database for studying the effect of resins on precipitation and the modeling of asphaltene–asphaltene and asphaltene–resin interactions. In a future publication, the effect of resins with different dipole moments and surfactants on asphaltene precipitation will be presented for different petroleum fluids.

Experimental

We use eight different petroleum fluids with API gravities in the range of 10 to 56 (see Table 1). Two of the petroleum fluids are from two different wells in the Hamaca field in Venezuela. The other petroleum fluids are from various parts of the world. Detailed composition of three crudes at ambient conditions is available in Table 2. In this work, asphaltenes are first precipitated from the petroleum fluids using n-C_5, n-C_7, and n-C_{10}, then resins are separated from the n-C_5 deasphaltened crude by: (1) precipitation with liquid propane, and (2) modified ASTM D-2007 (1991a) adsorption procedure. In the adsorption method, the oils are eluted with five different n-C_5/toluene volume ratios.

Table 1. Crude Data

Crude	Density at 20°C (g/cm^3)	API Gravity at 20°C	Refractive Index at 20°C	Description
H	1.0089	9	—	Very heavy
TE	0.9990	10	—	Very heavy
C	0.8588	33	1.487	Medium
TA	0.8372	37	1.479	Medium
TK	0.8520	35	1.488	Medium
S	0.8627	32	1.472	Medium
U	0.8550	34	1.491	Medium
B	0.7554	56	1.431	Very light

— ≡ not measured.

The dipole moment determination is made by measuring the dielectric constant, refractive index, and density of dilute solutions of asphaltenes, resins, and oils in toluene. The procedure is similar to Maruska and Rao's (1987); however, we use lower concentrations of polar solutes to allow a visual reading of the refractive index and to reduce the effect of association.

There has been a debate if n-C_5 asphaltenes are less polar than n-C_7 asphaltenes or vice versa (Speight, 1999). We separate the asphaltenes with both n-alkanes to clarify the issue of polarity by measuring the dipole moment. Furthermore, in the adsorption method, we opt to work with n-C_5 deasphaltened crudes instead of n-C_7 deasphaltened crudes, because

Table 2. Composition of Selected Crudes at Ambient Conditions

	Crude					
	C		TK		U	
Fraction	Comp. mol %	M g/mol	Comp. mol %	M g/mol	Comp. mol %	M g/mol
C_1	0.00	0.00	0.00	0.00	0.00	0.00
C_2	0.00	0.00	0.01	30.1	0.04	30.1
C_3	0.00	0.00	0.15	44.1	0.73	44.1
C_4	0.82	58.1	0.85	58.1	4.15	58.1
C_5	2.12	72.1	2.48	72.1	6.00	72.1
C_6	3.84	86.2	4.91	85.8	8.33	85.8
C_7	5.18	100.2	8.39	95.8	80.75*	—
C_8	7.32	114.2	11.14	108.5		
C_9	6.58	128.3	10.29	123.2		
C_{10}	6.11	142.3	7.83	137.8		
C_{11}	5.77	156.3	5.67	148.3		
C_{12}	4.99	170.3	4.38	154.4		
C_{13}	5.17	184.4	4.46	172.4		
C_{14}	4.81	198.4	3.79	187.9		
C_{15}	4.61	212.4	3.59	197.2		
C_{16}	3.72	226.4	3.02	210.1		
C_{17}	3.63	240.5	2.69	227.1		
C_{18}	3.48	254.5	2.62	240.9		
C_{19}	2.72	268.5	2.42	254.2		
C_{20^+}	29.13	433.6	21.31	441.2		
Total	100.00	242.0	100.00	206.1	100.00	—

* ≡ C_7 +

— ≡ not available

the latter would leave the C_5–C_7 fraction of asphaltenes soluble with resins.

All chemicals are reagent grade except propane (commercial grade). Once fractions are recovered, the solvent is evaporated under low vacuum. The fractions are then dried and weighed (within 0.01 g accuracy) using an analytical balance.

Asphaltene precipitation

From the examination of the various asphaltene precipitation methods and the identification of optimum separation conditions (Speight et al., 1984), we select the Syncrude analytical method (1979) with some modifications. The precipitation sequence includes mixing the crude with toluene (10 mL/g asphaltene in the crude) followed by an addition of n-C_5 (50 mL/mL toluene). The settling time is set to 12 h to allow complete precipitation. Asphaltenes are filtered under a vacuum using a Whatman glass microfibre filter paper (7 mm diameter and 1.5 μm pore size). The sequence is repeated several times to remove resins adsorbed onto asphaltenes until the liquid filtrate is colorless.

Apparatus. The experimental setup consists of a filtration flask and funnel connected to a vacuum pump through rubber tubings. To avoid solvent infiltration into the pump, a trap is used at a temperature of −60°C to liquefy pentane from vapor.

Resin adsorption. Once asphaltenes are removed, resins are separated from the deasphaltened oil using the ASTM D-2007 (1991a) method with some modifications. The deasphaltened crude is charged into an adsorption column containing attapulgus clay immersed in n-pentane. We use the following n-C_5/toluene volume ratios: 100/0, 85/15, 70/13, 50/50, and 0/100 to elute the oils. The elution continues until the yellow coloration of the liquid leaving the column reduces appreciably (the yellow coloration is attributed to aromatic hydrocarbons in oils). The column is then drained from solvent and resins are desorbed using a 40/40/20 volume mixture of toluene–acetone–methylene chloride.

Apparatus. The adsorption column (300 mm height × 44 mm diameter) is made of glass and contains attapulgus clay (250–500 μm pore size) with a sample/clay ratio of approximately 1/20 (wt/wt). The high quality of the clay (azobenzene equivalence value of 30–35) assures good selectivity and reproducibility of the tests.

Resin precipitation

We use a high-pressure cylinder with a piston connected to a high-pressure filter holder at one side, and a water pump at the other side. The filter holder contains a Whatman glass microfibre (4.7 mm diameter and 0.8 μm pore size) filter paper. Liquid propane from a 1-gal high-pressure bottle is charged at a low temperature (−5 to 0°C) into the cylinder containing the deasphaltened oil sample, with a sample propane ratio of 1/20 (wt/wt). The pressure in the cylinder is increased to 1400 psi and the mixture is left for 4–6 h at room temperature. A piston is then used to push the mixture through the filter. The resins are recovered from the filter as well as the cylinder walls by washing with toluene.

Apparatus. The cylinder used is made of stainless steel (400 mm long × 20 mm ID) and can stand a maximum pressure of 680 atm. Stainless steal tubings (1/16-in. ID) are used for connections to the water pump (max pressure 272 atm) and to the high-pressure filter holder. Ball valves (max pressure 136 atm) and needle valves (max pressure 408 atm) control the flow rate. The pressure of water pumped into the cylinder is read from a pressure gauge (max pressure 272 atm). The filter holder (stainless steel, 47 mm size) is designed to stand pressures up to 95 atm.

Dielectric constant

In a class of substances called insulators or dielectrics, the electrons move a very small distance from the nucleus when the substance is subjected to an electric field. The dielectric constant of a dielectric substance is a measure of chemical composition and density (Feynman, 1964). When a condenser containing a dielectric substance is subjected to an electric field, the dielectric constant is given by $\epsilon_r = C/C_0$, where C and C_0 are the capacitance of the condenser filled with the dielectric and air, respectively. In this work, a liquid test fixture is used as a condenser. The determination of capacitance is performed through impedance measurements (Hewlett-Packard, 1999). The electronic circuit makes up the liquid fixture connected to an LCR meter that measures the inductance L, the capacitance C, and the resistance R of the circuit. The choice of the equipment is driven by the frequency coverage, measurement range, accuracy, and ease of operation.

Apparatus. We use a precision LCR meter (HP 4284A) (20 Hz to 1 MHz frequency range) connected to a liquid test fixture (HP16452A) through 1-m long test leads (HP 16048A). The capacity of the liquid test fixture is 3.4 mL. For accurate reading of capacitance, the equipment is calibrated to account for lead capacitance. Measurements are performed at a frequency of 800 Hz and a voltage level of 1 V.

Refractive index

For a nonabsorbing medium, the refractive index is the ratio of the velocity of light in the vacuum to the velocity of light in the medium (Bitter, 1956). In the visible range of frequencies, measurements of the refractive index of the sodium D-line of light are possible using a refractometer. The effective speed of light is different in different materials, and on this basis, the refractive index depends on the nature of the material (Feynman, 1964).

Apparatus. We used an Abbe C-10 refractometer to measure the refractive index of liquid mixtures to be described later. A built-in thermometer allows the reading of the temperature. The refractive index range covered is 1.300 to 1.700, with an accuracy of 0.0003. Calibration is performed with naphthalene bromide, which has a refractive index of 1.656 at 25°C.

Density

The density of a substance is its mass per unit volume. The density is usually measured using pycnometers; however, digital density-meters, when available, provide more accurate data. In this work, density is measured using two types of pycnometers with a fixed volume. Density and refractive index are temperature-dependant. Density at a given temperature can be estimated from measurements at another temperature using the correlations of Van Ness and Van Westen (1951).

Apparatus. The density is measured using a weld-type pycnometer devised for the specific gravity of volatile liquids with an accuracy of 0.001 g/cm^3. The pycnometer made of borosilicate glass, has a capacity of 25 mL and is equipped with a glass stopper and a cap to reduce evaporation of the sample. The density of oils is measured with a Moore-Van Slyke specific-gravity bottle with ground-in stopper. The bottles made of borosilicate glass have a capacity of 2 mL.

Theory of Dipole Moment of Molecules

In a dipolar molecule, the center of negative charges (say electrons) and the center of positive charges (say protons) do not coincide. In such molecules, the charge multiplied by the separation between the centers is called dipole moment (Feynman, 1964). Large molecules containing heteroatoms such as *ms*-tetraphenylporphine do not necessarily possess a dipole moment when they have a symmetrical structure (Kumler, 1942). For nonsymmetrical molecules, the dipole moment is the vector (directed from the negative to the positive charge) that tends to orient a molecule in a polarized dielectric. The dipole moment is generally given in debye (1 D $= 3.338\times10^{-30}$ C·m); it is given by

$$\boldsymbol{\mu} = \sum_i e_i \boldsymbol{r}_i \tag{1}$$

where i refers to the number of atoms in the molecules, e_i is the charge of an atom in the molecule, and $\boldsymbol{r}_i$ is the distance vector between charges. The charge distribution creates an electric field that tends to line up the individual dipoles to produce a net moment per unit volume called electric polarization. The electric polarization, $\boldsymbol{P}$, is given by

$$\boldsymbol{P} = N\boldsymbol{\mu} \tag{2}$$

where N is the number of molecules per unit volume.

One can study the behavior of dielectrics in a condenser to estimate the electric properties. Dielectrics, such as crude oils are insulators; such materials do not conduct electricity, but when placed in a small electric field, molecules become polarized. When an electric field is applied, the charges that build on the plates of the condenser are two types: free charges, and polarization charges (of the opposite sign) due to polarization; the net charge on the plates will be the difference between the two. The charge density due to polarization is equal to the electric polarization inside the dielectric (Feynman, 1964). The dielectric constant is a characteristic of the dielectric, and is given by

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \tag{3}$$

where ϵ is the permittivity of the dielectric and ϵ_0 is the permittivity of the vacuum (equals 854×10^{-12} C^2/J/m or $1.11\times10^{-10}/4\pi$, F/m). The dielectric constant depends on the frequency ν and is written in the complex space as

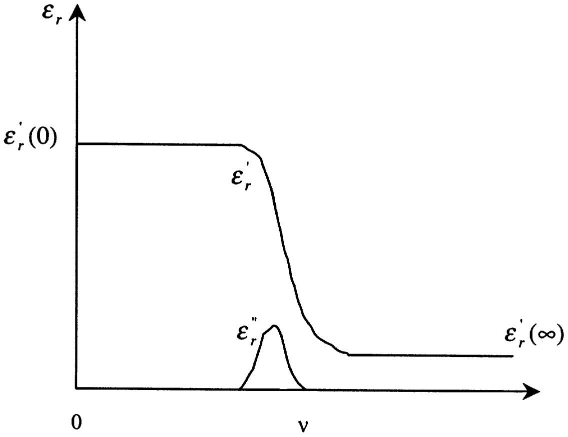


Figure 1. Dielectric constant vs. frequency.

$$\epsilon_r(\nu) = \epsilon_r'(\nu) - i\epsilon_r''(\nu) \tag{4a}$$

$$\epsilon_r(\nu) = \begin{cases} \epsilon_r'(0) & \text{at radio } \nu \quad (4b) \\ \epsilon_r'(\infty) = n^2 & \text{at visible } \nu \quad (4c) \end{cases}$$

where ϵ_r' and ϵ_r'' are the dielectric storage and loss, respectively (see Figure 1). The dielectric storage is the amount of polarization created at a given frequency and helps to determine the nature of the constituent material. The dielectric loss represents the energy of molecules dissipated or lost as heat; it is used to estimate the penetration of the sensing wave into the material (Sen et al., 1992; Pedersen et al., 1999). At radio frequency, the dielectric constant equals the dielectric storage at zero frequency; it is also called static dielectric constant $\epsilon_r'(0)$. At visible frequency, the dielectric constant is approximated by the dielectric storage at infinite frequency $\epsilon_r'(\infty)$; it is equal to the square root of the refractive index n of the sodium D-line of light (Maxwell, 1954).

Using fundamental electrostatic equations, one can readily derive the following expression that relates electric polarization to electric field $\boldsymbol{E}$

$$\boldsymbol{P} = \frac{(\epsilon_r - 1)}{4\pi}\boldsymbol{E} \tag{5}$$

The dipole moment cannot be measured directly. Several theories exist to relate the dipole moment to macroscopic measurable quantities, such as dielectric constant, refractive index, and density. The first theory from Clausius and Mosotti (Böttcher, 1952) is applicable to nonpolar molecules. Debye (1929) extended the formulation of Clausius and Mosotti to polar gases and liquid solutions. Later, Onsager (1936) advanced the original Clausius and Mosotti theory for polar molecules and proposed a new formulation. In the following, we present a brief review of these theories.

Clausius and Mosotti theory

Clausius and Mosotti used the notion of an internal field to relate the dielectric constant of a nonpolar spherical molecule to the density (Böttcher, 1952; Born and Wolf, 1980). While the electric field is the mean field obtained by averaging over a region that contains a large number of molecules, the internal (or effective) field acts on the molecule itself. The difference between the two fields is due to the gaps between molecules (Born and Wolf, 1980). To estimate the internal field, each molecule is considered to be surrounded by a small sphere. For nonpolar molecules, molecules inside the sphere do not produce any resulting field at the central molecule, and one can regard the molecule as being situated in a spherical region, inside which there is a vacuum and outside there is a homogeneously polarized medium. The internal field is derived by assuming that the field at the spherical hole is equal to the difference between the field at any point in the dielectric and the field due to a spherical plug. The expression for the internal field $\boldsymbol{F}$ is given by

$$\boldsymbol{F} = \boldsymbol{E} + \frac{4\pi}{3}\boldsymbol{P} \tag{6}$$

In vacuum, the internal field equals the electric field, but in other materials, it is higher. Clausius and Mosotti assumed that the electric dipole moment induced in a molecule is proportional to the internal field

$$\boldsymbol{\mu}_{\text{ind}} = \alpha \boldsymbol{F} \tag{7}$$

where α is the polarizability of the molecule, a macroscopic quantity that has the unit of volume (Smyth, 1955). The polarizability is a measure of the strength with which protons in the nucleus attract the electrons and prevent their distortion by the applied field. This parameter increases with increasing the atomic number, atomic size, and the ease of excitation of atoms in the molecules (Atkins, 1978). When N molecules are contained in a unit volume, one can write

$$\frac{4\pi a^3}{3} N = 1 \tag{8}$$

where a is the radius of the spherical molecules. Combining Eqs. 2, 5, 6 and 7

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{4\pi}{3} N\alpha \tag{9}$$

Equation 9 is the general expression of Clausius and Mosotti. Combining Eqs. 4c, 8 and 9

$$\alpha = \frac{n^2 - 1}{n^2 + 2} a^3 \tag{10}$$

The polarizability (also dipole moment) can have two contributions, depending on the nature of the molecule and the frequency of excitation: (1) permanent (orientation), and (2) induced. Polar molecules experience both contributions at very low frequencies (such as radio frequencies), while nonpolar molecules experience only the induced one. The induced contribution is the result of two parts: (1) atomic (or distortion), and (2) electronic effects. The former is associated with the molecular vibrations and the latter results from the displacement of the electron cloud by the field in the visible–ultraviolet frequency domain. The atomic polarizability is not readily determined and can be neglected on the grounds that it is small or is partially compensated by the use of the refractive index of the sodium D-line of light to estimate the electronic polarizability (or dipole moment).

Limitations. The Clausius and Mosotti equation applies to gases at moderate pressures, but deviations may occur at high pressures when the polarizability of molecules is large. There may also be some deviations for liquids, especially for mixtures (Böttcher, 1952).

Debye theory

Debye (1929) borrowed the oldest model of conductive spheres proposed by Clausius and Mosotti. He made the implicit assumption that the average permanent dipole moment of a molecule is proportional to the internal field. In the absence of external forces, the moments of a number of molecules will, on average, be distributed with the same probability over all directions in space. Therefore, when we consider a small solid angle at a given orientation, the average dipole moment is, according to Debye, equal to the total dipole moment divided by the number of molecules in the direction confined within the solid angle. Debye used the Boltzmann–Maxwell distribution law to calculate the small variations of the number of molecules confined within the solid angle. The final expression of the average dipole moment found is

$$\mu = \left(\alpha + \frac{\mu^2}{3kT}\right) F \tag{11}$$

where F is the magnitude of the internal field vector. Combining Eqs. 2, 5, 6, 8, 10 and 11 gives the Debye equation

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{n^2 - 1}{n^2 + 2} + \frac{4\pi N}{9kT}\mu^2 \tag{12}$$

It is more convenient to work with molar polarization P_M because of its additivity in mixtures (Debye, 1929; Böttcher, 1952; and Smyth, 1955). The molar polarization is defined by

$$P_M = \frac{\epsilon_r - 1}{\epsilon_r + 2}\frac{M}{\rho} \tag{13}$$

From the expression of the number of molecules per unit volume

$$N = \frac{N_A \rho}{M} \tag{14}$$

Combining Eqs. 12, 13 and 14, one can write

$$P_M = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho} + \frac{4\pi N_A}{9kT}\mu^2 \tag{15}$$

The first term on the righthand side of Eq. 15 is the induced molar polarization, and the second term is the orientation molar polarization. Therefore

$$P_M = P_{\text{ind}} + P_\mu \tag{16}$$

Limitations. At moderate pressures, the dielectric constant of a gas conforms accurately to the Debye equation. The dipole moment is generally determined from temperature variation. The procedure consists of plotting the molar polarization against $1/T$ and deducing the dipole moment from the slope of the straight line. For polar liquids, the dipole moment is usually overestimated and the theory does not hold. Several authors claimed that the limitations of the Debye equation are due to association between polar molecules (Böttcher, 1952). To overcome this deficiency, it was suggested one work with a very dilute solution of polar solutes in a nonpolar solvent. A series of differentiation techniques was proposed to measure the dipole moment of polar liquid solutions.

Differentiation Methods. The Debye theory was recast according to the modifications introduced by various authors. We retain only the methods in which the electronic molar polarization of the polar molecule is not required. The selected methods are those proposed by Cohen-Henriquez (Böttcher, 1952), LeFèvre (1948), Smyth (1950), and Guggenheim (1951). Measurements are performed with dilute solutions of a polar solute (species 1) in a nonpolar solvent (species 2). The methods consider the additivity of molar polarization and molecular weight, and assume linear variations of the dielectric constant, refractive index (and density in some cases) with the mole or weight fraction of the solute, as shown in Table 3. The authors listed in Table 3 expressed the difference between the molar polarization at a low frequency and at visible frequency in order to eliminate the solvent and the electronic polarization of the solute. The expression obtained is then differentiated with respect to mole (or weight) fraction of the solute at very low concentrations; the expressions of the orientation molar polarization of the solute are obtained (see Table 3). The equation of Smyth is similar to the one by LeFèvre, except that the density term is neglected. Guggenheim further simplified Smyth's equation by assuming that the dielectric constant of the solvent is approximately equal to the square of its refractive index. Böttcher found that the last three methods give similar results (1951). We select the Guggenheim version for its simplicity. We also select the Cohen-Henriquez equation and compare it with the one by Guggenheim.

Onsager theory

Because the internal field depends on the orientation, Onsager (1936) proposed to compute the orienting force-couple for each individual direction of the dipole. Onsager considered the original Clausius and Mosotti theory of the internal field not applicable to permanent dipoles. In his work, the total dipole moment is the vector sum of the permanent and the induced dipole moments

$$\boldsymbol{m} = \mu \boldsymbol{u} + \alpha \boldsymbol{F} \tag{17}$$

where μ is the permanent dipole moment in vacuum (which rotates around a mean orientation) and $\boldsymbol{u}$ is the unit vector in the direction of the dipole axis. In addition, the internal field is the sum of a cavity field and a reaction field

$$\boldsymbol{F} = \boldsymbol{G} + \boldsymbol{R} \tag{18}$$

where $\boldsymbol{G}$ is the cavity field and $\boldsymbol{R}$ is the reaction field. The reaction field is parallel to the average dipole moment and it is only the cavity field that contributes to the orientation of the polar molecule. Onsager solved the electrostatic problem by combining the results of a dipolar molecule in a nonpolarized dielectric with those of a spherical cavity in a polarized dielectric. The internal field is then expressed as [detailed derivations are provided by Onsager (1936)]

$$\boldsymbol{F} = \left(1 + \frac{n^2(\epsilon_r - 1)}{2\epsilon_r + n^2}\right)\boldsymbol{E} + \frac{\mu}{a^3}\,\frac{2(\epsilon_r - 1)}{2\epsilon_r + 1}\,\frac{(n^2+2)(2\epsilon_r+1)}{3\left(2\epsilon_r + n^2\right)}\boldsymbol{u} \tag{19}$$

Table 3. Differentiation Methods of Debye Equation for Binary Mixtures of Polar Solute (species 2) in Nonpolar Solvent (species 1)

Author	Assumptions	Orientation Molar Polarization	Eq.
Cohen-Henriquez	$\epsilon_r = ax_2 + \epsilon_{r_1}$	$P_{\mu_2} = \frac{3M_1}{\rho_1(n_1^2+2)^2}(a - 2n_1 c)$ $n = cx_2 + n_1$	(T1)
LeFèvre	$\epsilon_r = \epsilon_{r_1}(aw_2+1)$	$P_{\mu_2} = \frac{3M_2}{\rho_1}(\frac{(1-b)(\epsilon_{r_1} - n_1^2)}{(\epsilon_{r_1}+2)(n_1^2+2)} + \frac{a\epsilon_{r_1}}{(\epsilon_{r_1}+2)^2} - \frac{cn_1^2}{(n_1^2+2)^2})$ $\rho = \rho_1(bw_2+1)$ $n^2 = n_1^2(cw_2+1)$	(T2)
Smyth	$\epsilon_r = \epsilon_{r_1}(aw_2+1)$	$P_{\mu_2} = \frac{3M_2}{\rho_1}(\frac{a\epsilon_{r_1}}{(\epsilon_{r_1}+2)^2} - \frac{cn_1^2}{(n_1^2+2)^2})$ $n^2 = n_1^2(cw_2+1)$	(T3)
Guggenheim	$\epsilon_{r_1} \approx n_1^2$	$P_{\mu_2} = \frac{3M_2}{\rho_1}\frac{\epsilon_{r_1}}{(\epsilon_{r_1}+2)^2}(a - c)$ $\epsilon_r = \epsilon_{r_1}(aw_2+1)$	(T4)

Table 4. Asphaltenes Precipitated by n-C_5, n-C_7, and n-C_{10} from Crudes

	Crude (wt %)							
Precipitant	H	TE	C	TA	TK	S	U	B
n-C_5	17.7	14.8	2.3	0.18	1.33	1.1	2.5	0.05
n-C_7	13.5	11.9	1.52	0.10	0.46	0.77	—	0.04
n-C_{10}	13.0	11.2	1.42	0.05	0.26	0.63	—	0.03

— ≡ not measured.

Table 6. Resins Adsorbed on Clay after Elution of Oils With n-C_5, n-C_7, and n-C_{10}

	Crude (wt %)							
Elution of Oils with	H	TE	C	TA	TK	S	U	B
n-C_5	30.3	28.6	6.5	6.0	7.5	3.5	8.6	0.56
n-C_7	31.1	28.7	7.4	6.2	7.6	3.8	—	0.65
n-C_{10}	32.0	30.0	7.8	6.5	7.9	4.0	—	0.68

— ≡ not measured.

Equations 6 and 19 are identical for nonpolar molecules (for which $\mu = 0$ and $\epsilon_r = n^2$). Unlike the induced dipole moment, the permanent dipole moment depends on the orientation of the molecule and its average value is equal to the actual dipole moment times the mean orientation of the molecule. The mean orientation is determined from the Boltzmann–Maxwell formula using the work of orientation. The expression derived by Onsager is then introduced into Eqs. 17–19 to give the Onsager equation

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{n^2 - 1}{n^2 + 2} + \frac{4\pi N}{9kT}\left(\frac{3\epsilon_r(n^2+2)}{\left(2\epsilon_r + n^2\right)\left(\epsilon_r + 2\right)}\mu^2\right) \qquad (20)$$

Equations 12 and 20 are identical for $\epsilon_r = n^2$. Therefore, the Onsager and Debye equations give similar results for nonpolar molecules. However, for polar molecules ($\epsilon_r > n^2$), the dipole moments calculated from Debye and Onsager equations are different.

Limitations. The formulation of Onsager is limited to spherical molecules in liquid systems. In addition, the neighborhood of a molecule is considered to be a continuum.

Results

The results are presented in three different parts. In the first part, the amount of asphaltenes precipitated with n-alkanes (n-C_5, n-C_7, and n-C_{10}) and resins separated by propane precipitation and the ASTM D2007 (1991a) adsorption method with different solvents are presented. In the second part, we provide the results of the dipole moment calculation from the Debye and Onsager methods for several chemicals with known dipole moments from the literature. We select the Onsager method and in the third part present the dipole moment of the asphaltenes, resins, and oils.

Asphaltene and resin amounts

Table 4 provides the results of asphaltene precipitation with n-C_5, n-C_7, and n-C_{10} from the eight petroleum fluids (from here on, we refer to petroleum fluids as crudes). The amount of n-C_5 asphaltenes varies from 0.05 wt % in crude B to 17.7 wt % in crude H and decreases with the carbon number of the precipitating n-alkane. In Table 5 we present the results of asphaltene and resin (that is, asphalt) precipitation by propane. When propane is mixed with the crude, C_3 asphaltenes and C_3 resins precipitate. However, when propane is mixed with the n-C_5 deasphaltened crude, C_3–C_5 asphaltenes and C_3 resins precipitate. Thus, the difference between the two amounts provides the n-C_5 asphaltenes in the crude (see Table 5). The difference compares well with the amounts of n-C_5 asphaltenes reported in Table 4. The disparity is due to some loss during the separation. Results of resin separation by the modified ASTM D2007 adsorption method (1991a) using different solvents are provided in Tables 6 and 7. Table 6 shows the amount of resins recovered after elution of oils with n-C_5, n-C_7, and n-C_{10}. The amount of resins slightly increases with the carbon number of n-alkane used to elute oils. For all the crudes, the amount of resins by adsorption are higher than those by propane precipitation. It is also observed that crudes with high asphaltene content contain substantial amounts of resins. Material balance calculation on the very heavy crudes reveals minor losses [that is, irreversible adsorption of polar compounds on the clay (<1 wt %)]. Table 7 provides the amount of resins recovered from the n-C_5 deasphaltened crudes after elution of oils with different n-C_5/toluene volume ratios of 85/15, 70/30, 50/50, and 0/100 (vol/vol). It is found that the amount of resins decreases with the volume of toluene in n-C_5/toluene mixtures. When using only n-C_5 to elute oils, we obtain almost two times more resins than when using only toluene. In order to compare our results with other separation techniques, the resin content of crude E has been determined in two different laboratories (Durandeau, 1999; Boduszynski, 2000). Durandeau used thin-layer chromatography (TLC) and reported a value of 14 wt %, while Boduszynski used high-performance liquid chromatography (HPLC) and

Table 5. Asphalt (asphaltenes and resins) Precipitated by Propane from Crudes and n-C_5 Deasphaltened Crudes

	Crude (wt %)							
Precipitation from	H	TE	C	TA	TK	S	U	B
Crudes	38.6	36.3	6.2	3.9	5.7	—	—	—
n-C_5 deasphaltened crudes	19.8	20.0	3.3	3.6	4.2	1.5	—	0.3
Difference	18.8	16.3	2.9	0.2	1.5	—	—	—

— ≡ not measured.

Table 7. Resins Adsorbed on Clay after Elution of Oils With Various n-C_5/Toluene Mixtures

	Crude (wt %)							
Elution of Oils with n-C_5/Toluene	H	TE	C	TA	TK	S	U	B
100/0 (vol/vol)	30.3	28.6	6.5	6.0	7.5	3.5	8.6	0.56
85/15 (vol/vol)	26.4	24.0	5.9	4.8	5.9	2.7	—	0.45
70/30 (vol/vol)	21.8	19.9	4.9	3.9	5.2	2.2	—	0.37
50/50 (vol/vol)	20.0	18.0	4.2	3.6	4.2	1.5	—	0.30
0/100 (vol/vol)	14.0	13.3	2.9	2.8	2.9	1.1	—	0.25

— ≡ not measured.

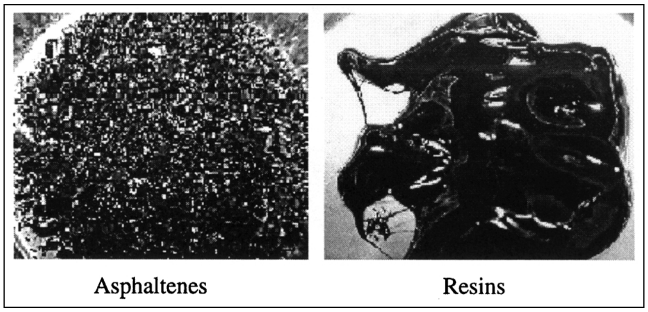


Figure 2. Asphaltenes and resins separated from crude H.

Table 8. Substances with Known Dipole Moments

Substance	Formula	M g/mol	$\rho^{20°C}$ g/cm^3	μ D
Toluene	C_7H_8	100.2	0.940	0.37
Dibutylamine	$C_8H_{19}N$	129.2	0.760	1.18
Anisole	C_7H_8O	108.1	1.000	1.36
Ethanol	C_2H_6O	46.1	0.790	1.69
Ethyl acetate	$C_4H_8O_2$	88.1	0.894	1.78
Ethyl benzoate	$C_9H_{10}O_2$	150.2	1.051	1.95
2-Butanone	C_4H_8O	72.1	0.800	2.78
Acetone	C_3H_6O	58.1	0.790	2.88
N,N-Dimethylformamide	C_3H_7NO	73.1	0.944	3.82
Dimethylsulfoxide	C_2H_6OS	78.1	1.096	3.96
3-Methyl-2-Cyclopenten-1-one	C_6H_8O	96.1	0.980	4.33

Source: Lide and Frederikse (2000); McClellan, (1963).

reported a resin content of 25 wt. %. In TLC, saturates are eluted with n-hexane and aromatics with toluene, while in HPLC, n-hexane is used to elute oils. The solvents used in the two techniques correspond to the extreme proportion of n-C_5/toluene volume ratios. The results from HPLC correspond to 100% n-C_5 (0% toluene) and the results from TLC correspond to 100% toluene (0% n-C_5) when compared with our adsorption method. It is interesting to see that the results from HPLC and TLC for resins, which are, respectively, 25 and 14 wt % for crude TE, are in line with our measurements of 28.6 wt % and 13.3 wt %, respectively. Later we comment on the true resin content of various crudes once the dipole moment of separated resins are presented.

Figure 2 shows the separated asphaltenes and resins from crude H. The resins are those separated by adsorption after elution of oils with n-C_5. We observe that asphaltenes and resins have very different appearances. Indeed, asphaltenes from all the crudes are black, shiny, and friable solids, while resins are dark brown, shiny, and gummy. Oils are orange/brown liquids with a density that varies from one crude to another. The color of oils changes from orange/brown to red/brown when we increase the proportion of toluene in the n-C_5/toluene mixtures. This change in coloration may suggest the presence of polar species in the oils (Becker, 2000).

Dipole moment verification

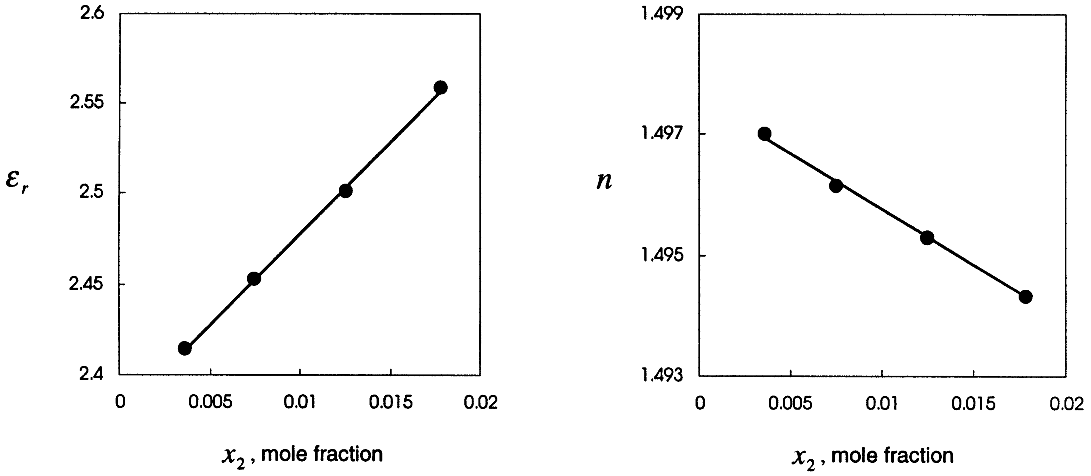
The methods presented for the estimation of the dipole moment of molecules are applied to 12 chemicals with known dipole moments from the literature (Lide and Frederikse, 2000; McClellan, 1963); see Table 8. The objective is to verify the validity of the methods; the most accurate method will be used to determine the dipole moment of asphaltenes, resins, and oils. In the selection of the chemicals, we aim to cover a wide range of dipole moments (0 to 4 D) as well as a variety of chemical functions (ketones, alcohols, amines, and so on).

The dipole moment of toluene, dibutylamine, anisole, ethanol, ethyl acetate, ethyl benzoate, and acetone were measured in the vapor phase by the temperature variation procedure in the microwave-frequency region, using the Debye equation (Lide and Frederikse, 2000; McClellan, 1963). The dipole moments of the remaining substances were measured in liquid solutions, with benzene at 20°C. For instance, the dielectric constant of 2-butanone solutions in benzene was measured by a bridge method and the dipole moment calculated from the LeFèvre (1948) equation. For dimethylsulfoxide, the dielectric constant was measured by a resonance method and the dipole moment was calculated from the Halverstadt−Kumler (1942) equation. Usually, the dipole moment measurements in the gas phase are the most reliable (McClellan, 1963).

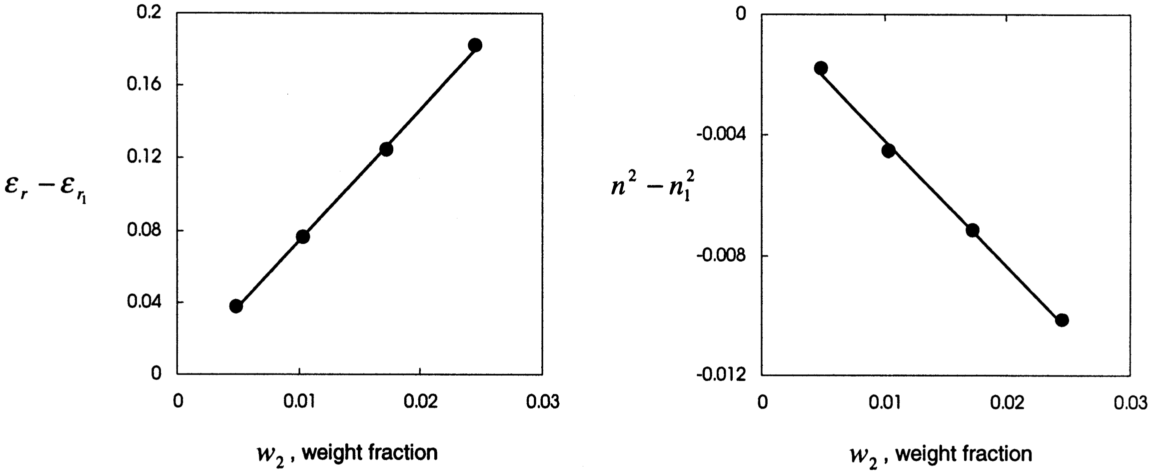
In our measurements, toluene is selected as a solvent, although it has a small dipole moment ($\mu = 0.4$ D). We found that the results did not differ significantly when using p-xylene ($\mu = 0$ D). Toluene is preferred because of the high solubility of asphaltenes, resins, and oils in this solvent. While preparing the solutions, we make sure that all the chemicals are dissolved in toluene. The dipole moment of the substances in Table 8 is calculated from various methods, using Eqs. T1 (Cohen-Henriquez) and T4 (Guggenheim) from Table 3, and Eq. 20 (Onsager). The atomic polarization is neglected in our calculations. Figure 3 presents results for the ethanol solution in toluene. The variation of the dielectric constant and refractive index of the solution with the mole fraction of ethanol in toluene is determined by the Cohen-Henriquez method. The Guggenheim method requires the determination of $\epsilon_r - \epsilon_{r_1}$ and $n^2 - n_1^2$ vs. the weight fraction of ethanol in toluene (ϵ_{r_1} and n_1 are the dielectric constant and refractive index of toluene, respectively). For the Onsager method, we present the variation of the dielectric constant and refractive index of ethanol solutions as a function of the weight percent of ethanol in toluene. In the Cohen-Henriquez and Guggenheim methods, the slope of the straight lines is substituted in the corresponding equations. For the Onsager method, the variations are extrapolated to $w_2 = 100$ wt % to determine the dielectric constant and refractive index of ethanol. The same procedure is applied to all substances, and the results are summarized in Table 8. For each method, we report the absolute relative error (%) of the dipole moment and the data from the literature.

Examination of the results in Table 9 reveals that the Cohen-Henriquez and Guggenheim methods overestimate the dipole moment of the substances in Table 8. The differences with data in the literature are very high, and can be as high as 80%. The error in estimation becomes large for substances with a high dipole moment. On the other hand, the Onsager equation underestimates the dipole moment. Deviations may arise from the extrapolation technique used, which produces

(a) Cohen-Henriquez



(b) Guggenheim



(c) Onsager

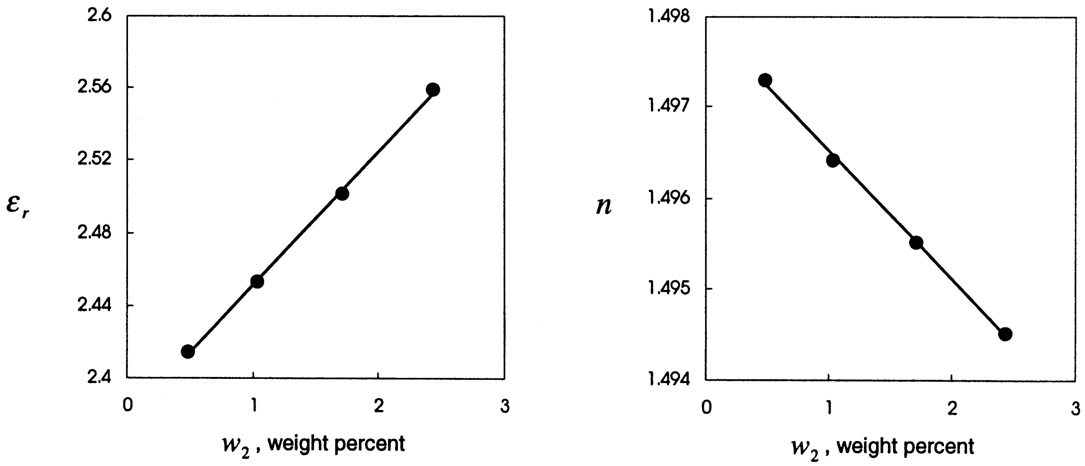


Figure 3. Dielectric constant and refractive index vs. concentration of ethanol in toluene.

Table 9. Dipole Moment of Substances Using Different Methods

	Calculated μ, D					
Substance	CH	Relative Error, %	G	Relative error, %	O	Relative Error, %
Toluene	0.35	−7	0.53	40	0.36	−3
Dibutylamine	0.86	−27	1.57	33	1.14	3
Anisole	1.57	14	1.93	40	1.13	−16
Ethanol	3.01	78	2.68	58	1.82	8
Ethyl acetate	2.23	25	2.76	55	1.75	−2
Ethyl benzoate	2.45	25	3.01	54	1.67	−14
2-Butanone	3.39	22	4.12	48	2.66	−4
Acetone	3.68	28	4.16	44	2.78	−4
N,N-Dimethylformamide	5.13	34	6.31	65	3.49	−7
Dimethylsulfoxide	5.76	45	7.11	79	3.49	−12
3-Methyl-2-cyclopenten-1-one	6.90	59	7.62	76	4.10	−5

Note: CH: Cohen-Henriquez; G: Guggenheim; O: Onsager.

some uncertainties in the results, especially for refractive indices. Nevertheless, the overall deviation with the Onsager method is small. We select this method for the determination of the dipole moment of asphaltenes, resins, and oils.

Dipole moment of asphaltenes, resins, and oils

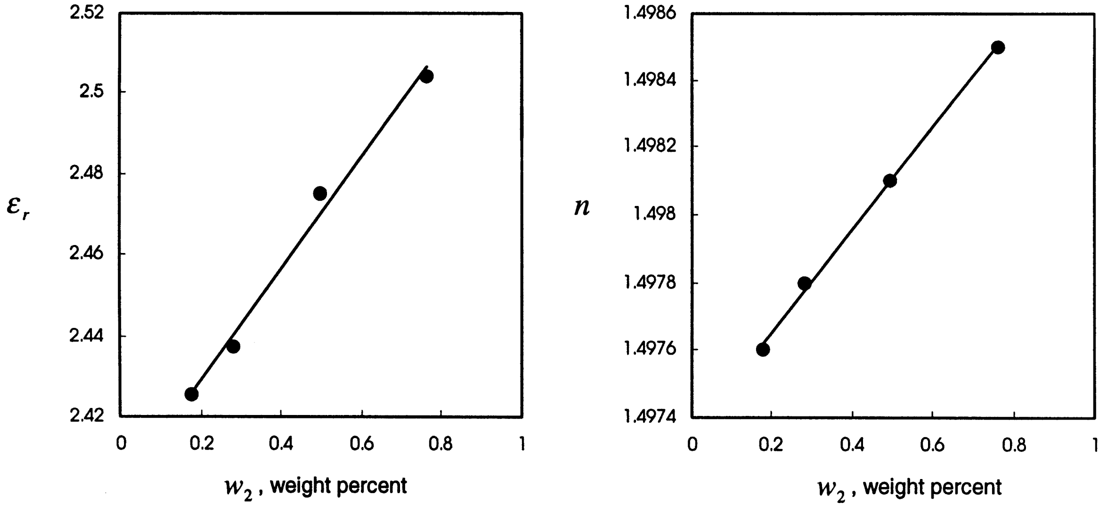
Following the preceding procedure, four different solutions with an increasing concentration of solute (that is, asphaltenes, resins, or oils) in toluene are prepared. The oils considered comprise only the hydrocarbons that are nonvolatile at atmospheric conditions; the light hydrocarbons were removed by evaporation. We use a small concentration of solutes (< 5 wt %) in order to allow a complete dissolution of asphaltenes and resins in toluene and for an accurate reading of refractive indices. For each sample, the tests are repeated two to four times to assure reproducibility of the results.

Among the parameters required in the dipole moment calculation are the molecular weight and density of asphaltenes and resins. The molecular weight of asphaltenes and resins is estimated by fluorescence depolarization spectroscopy according to the procedure described by Groenzin and Mullins (2000). The average molecular weights are approximately 900 for asphaltenes and 700 amu for resins. The density is assumed to be 1.2 g/cc for asphaltenes (Schabron and Speight, 1998; De Hemptinne et al., 1999) and 1.0 g/cc for resins (Wu et al., 2000). For oils, the density and refractive index are measured at 20°C and the molecular weight is calculated using the Riazi and Daubert (1987) correlation.

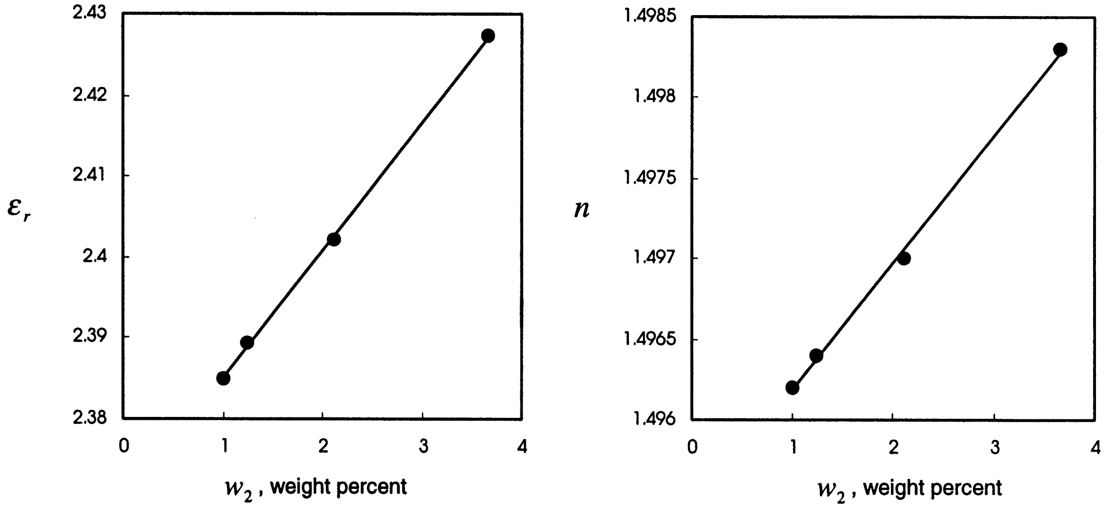
Figures 4 and 5 illustrate the variation of the dielectric constant and refractive index of n-C_5 asphaltenes, resins, and oils for the very heavy crude H and the very light crude B, respectively. The linear variations are extrapolated to w_2 (weight fraction in toluene) of 100 wt % to estimate the dielectric constant and refractive index of asphaltenes, resins, and oils. The small range of variation of w_2, especially for asphaltenes, increases the uncertainty in the extrapolation results. The dielectric constant of asphaltenes, resins, and oils are calculated with a maximum error of 2%. The error on the estimation of refractive index of asphaltenes and resins increases because of the extrapolation; however, it does not exceed 1%. Oils are viscous translucent liquids and their refractive index can be measured directly with an error of about 0.1%. The data obtained by direct measurement and extrapolation from oils in toluene solutions compare very well. The dielectric constant and refractive index of asphaltenes, resins and oils are reported in Table 10 along with the density and molecular weight. The dielectric constants of asphaltenes, resins, and oils are in the ranges of 5.5−18.4, 3.8−5.1, and 2.1−2.6, respectively. The range of variation of the refractive index is 1.638−1.707 for asphaltenes, 1.576−1.608 for resins, and 1.472−1.527 for oils. The refractive indices of asphaltenes are in line with those reported in the literature (see Table 11). However, some measured dielectric constants of asphaltenes (crudes H, TE, C, and TK) are high compared to 6−7 range in the literature in Table 11. Oudin (1970) measured the dielectric constant of asphaltenes in chloroform at a concentration of 20 g/L and reported a value of 6.2 for asphaltenes soluble in CCl_4 and 6.9 for asphaltenes insoluble in CCl_4. Maruska et al. (1987) measured the dielectric constant of asphaltenes in toluene at a concentration of 1−100 g/L and reported a value of 6.8. We measured the dielectric constant of asphaltenes in toluene at a concentration of 1−8 g/L and obtained dielectric constants in the range of 5.5−18.4. In this work, the asphaltene concentrations in toluene are low compared to those used by Maruska et al. and Oudin. This suggests that the high dielectric constants measured in our work may not be due to an association between molecules.

Table 12 provides the dipole moment of asphaltenes, resins, and oils calculated with the Onsager equation. The dipole moments are in the 3.3−7.0 D range for n-C_5 asphaltenes. It is found that the dipole moment of asphaltenes increases with the carbon number of the precipitating n-alkane. The results show that n-C_7 asphaltenes are more polar than n-C_5 asphaltenes (note that we have used the same molecular weight for both n-C_5 and n-C_7 asphaltenes). Previous studies by Nighswander et al. (1993), Speight (1999), and Nalwaya et al. (1999) suggest that the molecular weight and the metal content of asphaltenes increases with the carbon number of the precipitating n-alkane, which is consistent with our dipole moment data. Table 12 provides the dipole moment of resins by precipitation and adsorption methods. Resins precipitated by propane are more polar than resins separated by adsorption. This reveals that propane precipitates only part of the resin fraction containing the most polar molecules. In the adsorption method, n-C_7 resins are more polar than n-C_5 resins, because they contain the C_5−C_7 fraction of as-

(a) n-C_5 Asphaltenes



(b) Resins



(c) Oils

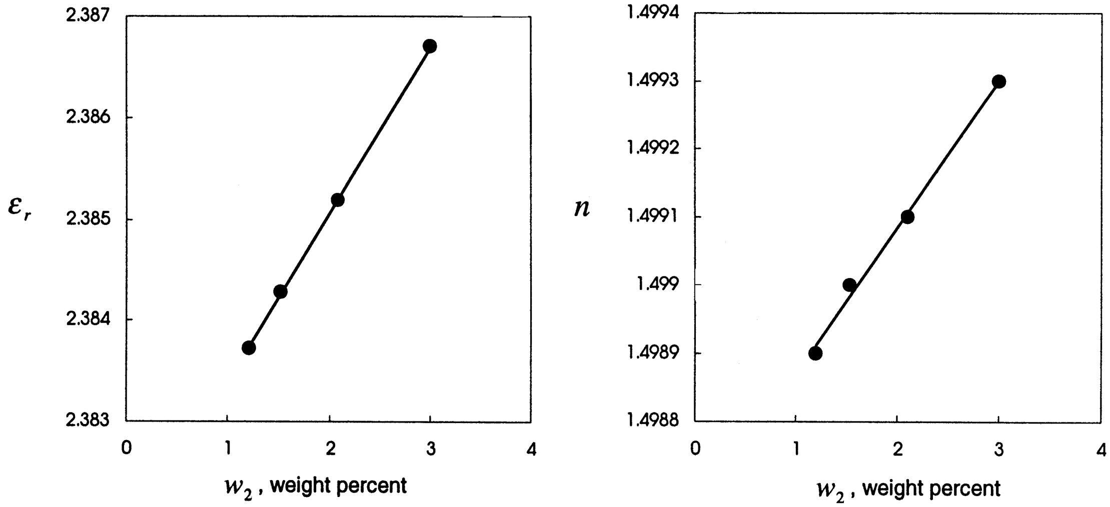
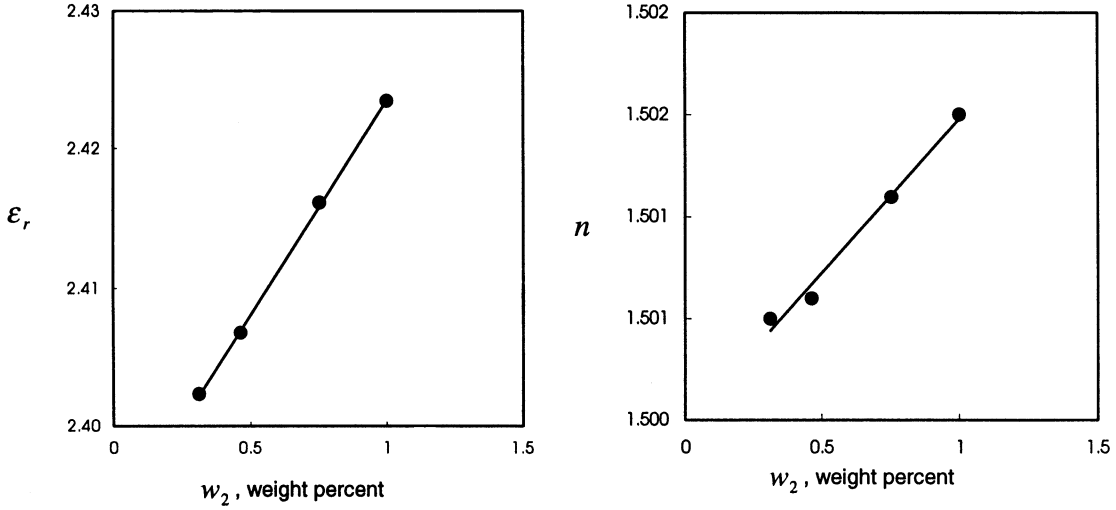
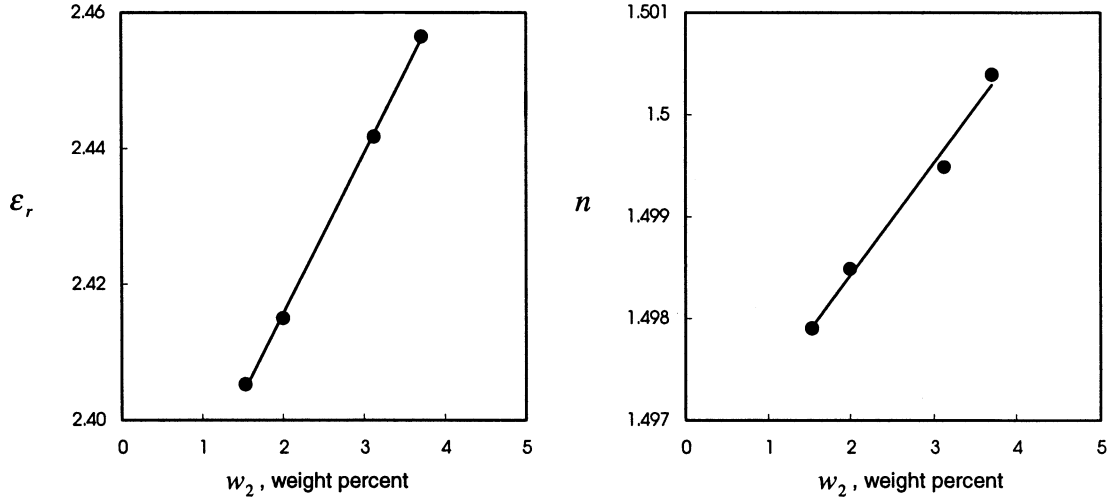


Figure 4. Dielectric constant and refractive index vs. concentration of n-C_5 asphaltenes, resins, and oils (eluted with n-C_5) in toluene for crude H.

(a) n-C_5 Asphaltenes



(b) Resins



(c) Oils

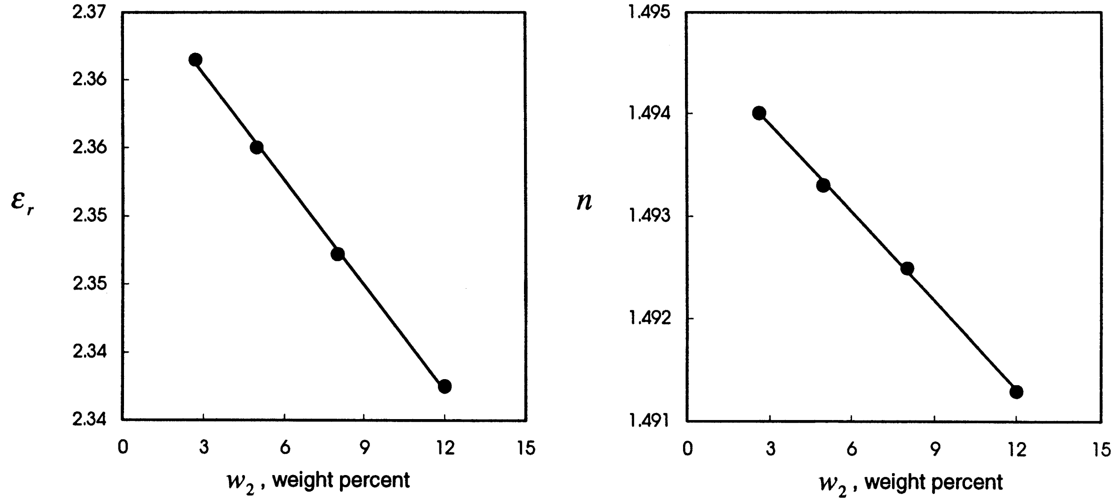


Figure 5. Dielectric constant and refractive index vs. concentration of n-C_5 asphaltenes, resins, and oils (eluted with n-C_5) in toluene for crude B.

Table 10. Dielectric Constant, Refractive Index, Density, and Molecular Weight of n-C_5 Asphaltenes, Resins, and Oils

	H	TE	C	TA	TK	S	U	B
				n-C_5 Asphaltenes				
$n^{20°C}$	1.647	1.707	1.638	1.676	1.706	1.668	1.685	1.650
ϵ_r	16.2	18.4	15.2	9.2	10.9	10.1	8.2	5.5
$\rho^{20°C}$, g/cm^3	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
M, g/mol	900	900	900	900	900	900	900	900
				Resins				
$n^{20°C}$	1.576	1.587	1.606	1.585	1.608	1.608	1.595	1.606
ϵ_r	3.9	3.8	5.1	4.8	4.5	3.9	3.8	4.7
$\rho^{20°C}$, g/cm^3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
M, g/mol	700	700	700	700	700	700	700	700
				Oils				
$n^{20°C}$	1.527	1.522	1.487	1.497	1.496	1.498	1.496	1.472
ϵ_r	2.6	2.5	2.2	2.3	2.4	2.4	2.4	2.1
$\rho^{20°C}$, g/cm^3	0.935	0.935	0.875	0.876	0.876	0.870	0.881	0.830
M, g/mol	371	389	269	287	300	290	320	196

Table 11. Dielectric Constant and Refractive Index of Asphaltenes and Resins

Source	Sample	ϵ_r	$n^{20°C}$
Oudin (1970)	n-C_5 Asphaltenes soluble in CCl_4	6.16	—
	n-C_5 Asphaltenes insoluble in CCl_4	6.92	—
	Resins	5.32	—
Maruska and Rao (1987)	n-C_5 Asphaltenes	6.8	1.682
Buckley et al. (1998)	n-C_6 Asphaltenes	—	1.720

— ≡ not reported.

phaltenes (that is, the fraction of asphaltenes soluble in n-C_7 but insoluble in n-C_5). When toluene is introduced into the eluting solvent of oils, even at small concentrations, the dielectric constant of resins increases linearly with the amount of toluene in the solvent as shown in Figure 6. The dipole moment of resins separated after elution of oils with various n-C_5/toluene volume ratios is given in Table 12. A gradual increase in the dipole moment is observed with the increasing volume of toluene. These results imply that toluene does elute some resins with oils, probably those weakly bound to the clay. A nitrogen analysis of the oils of crudes H and C shows that the resins eluted by toluene are those containing nitrogen functions (see Table 13). Therefore, it is recommended that toluene not be used with n-C_5 to separate oils from resins. In fact, the oils eluted by pure n-C_5 possess a small dipole moment that does not exceed 1 D (see Table 12). In order to elucidate the origin of this dipole moment, we used distillation cuts from two different crudes (an asphaltic crude and a waxy crude). The asphaltic crude is heavy and viscous with high sulfur, asphaltene, resin and aromatic content (> 50 wt %). The waxy crude contains large amount of paraffins and small amount of aromatics. The asphaltene

Table 12. Dipole Moment (in debye) of Asphaltenes, Resins and Oils

	Crude							
	H	TE	C	TA	TK	S	U	B
				Asphaltenes				
Precipitated by								
n-C_5	6.9	7.0	6.7	4.8	5.2	5.1	4.4	3.3
n-C_7	7.2	7.7	7.2	5.8	6.5	6.4	—	4.0
				Resins				
Precipitated by								
C_3	4.0	3.8	4.4	3.5	4.0	4.2	—	3.7
Adsorbed after elution of oils with								
n-C_5	2.5	2.4	3.2	3.1	2.8	2.4	2.4	3.0
n-C_5/toluene, 85/15 vol/vol	2.6	2.5	3.3	3.1	3.0	2.5	—	3.1
70/30 vol/vol	2.7	2.6	3.5	3.2	3.1	2.6	—	3.2
50/50 vol/vol	2.9	2.8	3.6	3.3	3.2	2.7	—	3.4
0/100 vol/vol	3.1	2.9	3.7	3.3	3.4	2.8	—	3.5
n-C_7	3.5	3.6	3.9	3.4	3.6	3.9	—	3.7
				Oils				
Eluted by								
n-C_5	0.9	0.8	0.0	0.4	0.6	0.7	0.7	0.0

— ≡ not measured.

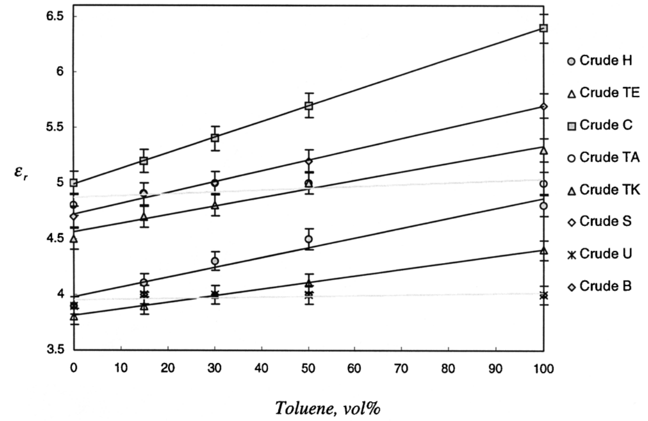


Figure 6. Increase of the dielectric constant of resins with the amount of toluene in the eluting solvent of oils.

Table 13. Nitrogen Cotent of Oils from Crude H and C Eluted with Various n-C_5/Toluene Mixtures

n-C_5/Toluene	Crude (ppm)	
(Vol/vol)	H	C
100/0	213	250
85/15	655	300
70/30	1,100	356
50/50	1,700	415

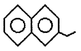
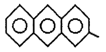
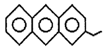
and resin content in waxy crudes is low (<10 wt %) (Whauquier, 1995). The dipole moment of the distillation cuts is determined and presented in Table 14. The cuts from the waxy crude are completely apolar, while the cuts from the asphaltic crude have dipole moments in the same range as the oils listed in Table 12. Moreover, it is unlikely that the distillation cuts up to 550°F contain traces of asphaltenes or resins. Asphaltic crudes are characterized by a high amount of aromatic hydrocarbons (Whauquier, 1995), and this may be the precursor of the small polarity measured. Although still a subject of controversy, we consider that slightly polar resins are distinguished from slightly polar aromatics in that the polarity of resins stems from the presence of heteroatoms in the molecule. Swanson (1942) reported the small polarity of oils and attributed it to the high electronic and atomic polarizations of heavy aromatic hydrocarbons.

The results just presented for different crudes show that the dipole moment is in the 3.3–7.0 D range for n-C_5 asphaltenes, 2.4–3.2 D for resins, and 0–0.9 D for oils. Water is a polar substance and its dipole moment is 1.87 D. Our dipole moment measurements show that in these crudes, asphaltenes, and to a lesser degree resins are highly polar molecules. Asphaltenes are more polar than resins in the same crude, although resins of one crude can be more polar than asphaltenes of another crude.

Table 14. Dipole Moment (in debye) of Distillation Cuts from Asphaltic Crude and Waxy Crude

Cut, °C	Asphaltic Crude	Waxy Crude
177–132	0.3	0.0
232–288	0.6	0.0
288–343	0.7	0.0
343–454	0.9	0.0

Table 15. Effect of Charge Separation on Dipole Moment

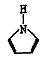
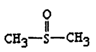
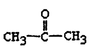
Molecule	Formula	μ, D
Toluene		0.4
Ethyl benzene		0.6
2-Methyl naphthalene		0.4
2-Ethyl naphthalene		0.6
2-Methyl anthracene		0.5
2-Ethyl anthracene		0.6

Source: Lide and Frederikse, 2000; McClellan, 1963.

Tables 15 and 16 show the effect of charge separation and the presence of heteroatoms on the dipole moment of several substances, respectively. The dipole moment slightly increases from toluene to ethyl anthracene (see Table 15), suggesting that charge separation does not contribute significantly to the dipole moment of asphaltenes. Table 16 provides the dipole moment of some chemicals that have been reported to be part of the asphaltenes (Waldo et al., 1992; Mitra-Kirtley et al., 1993). The presence of certain groups (such as sulfoxide) in a molecule has a significant effect on the dipole moment.

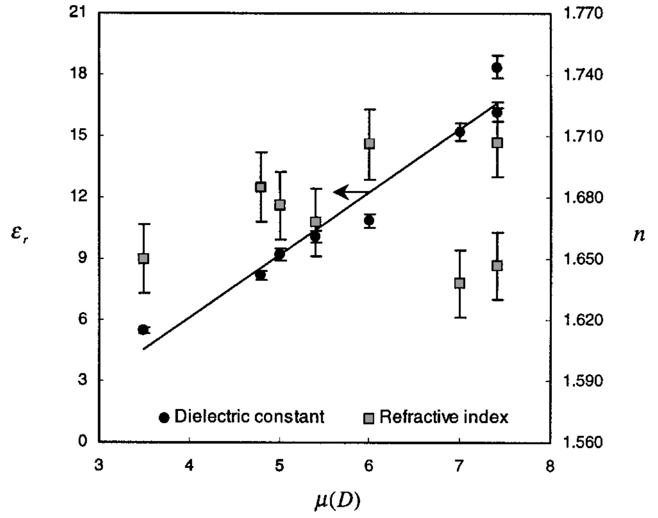
Figure 7 illustrates the variation of the dielectric constant and refractive index of n-C_5 asphaltenes and resins from adsorption vs. the dipole moment. There is a linear relationship

Table 16. Effect of Heteroatoms on Dipole Moment

Molecule	Formula	μ, D
1.H-Pyrrole		1.7
Pyridine		2.2
Dimethyl sulfoxide	 $CH_3-\overset{O}{\overset{\|}{S}}-CH_3$	4.0
Thiophene		0.6
Dimethyl sulfide	CH_3-S-CH_3	1.6
Phenol		1.2
Acetone	 $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	2.9

Source: Lide and Frederikse, 2000; McClellan, 1963.

(a) n-C_5 Asphaltenes



(b) Resins

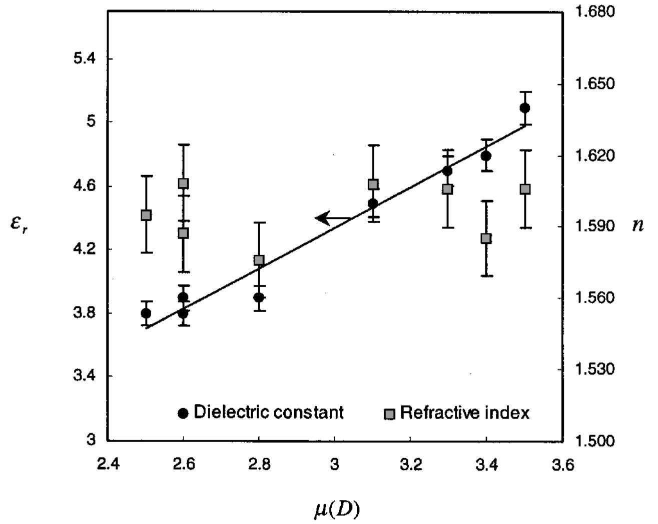


Figure 7. Dielectric constant and refractive index vs. dipole moment of n-C_5 asphaltenes and resins.

between the dielectric constant and dipole moment for both asphaltenes and resins. However, no correlation is observed between the refractive index and the dipole moment of these fractions. A close examination of Figure 7 shows that the refractive index is around 1.68 for asphaltenes and 1.60 for resins. The refractive index has been previously used to determine the onset of asphaltene precipitation from crudes (Buckley, et al., 1998), and it was concluded that asphaltene precipitation is dominated by London dispersion interactions. In a separate study on the effect of resins/surfactants on asphaltene precipitation (work to be published in the near future), we demonstrate that the effect of resins on asphaltene precipitation is a function of their dipole moment. In the same work, the onset of asphaltene precipitation is found to increase when resins or surfactants are added to the crude; the magnitude of the increase as well as the amount of precipitation depend on the dipole moment of the added resin/surfactant. These measurements suggest that dipole–dipole interactions should be included in the study of asphaltene precipitation from crudes.

Conclusions

Based on extensive work on the separation of asphaltenes and resins from petroleum fluids and the measurement of the dipole moment of asphaltenes, resins, and oils, we draw the following conclusions.

1. Asphaltenes precipitated by heavy normal alkanes are more polar than asphaltenes precipitated by light normal alkanes; n-C_{10} asphaltenes are more polar than n-C_7 asphaltenes, and n-C_7 asphaltenes are more polar than n-C_5 asphaltenes.
2. The propane precipitation method separates only part of the resins. This part is the most polar fraction of the resins.
3. The total resins can be precipitated by adsorption using n-C_5 deasphaltened crude. Use of an aromatic solvent such as toluene with n-C_5, even a small quantity, may reduce the amount of the separated resins.
4. For a variety of crudes used in this study, the dipole moment of resins and asphaltenes are in the ranges of 2–3 D and 3–7 D, respectively.
5. For all the crudes used in this study, the asphaltenes are more polar than the resins in the same crude. However, resins from one crude could be more polar than the asphaltenes in another crude.
6. The oil fraction (that is, the atmospheric crude minus the asphaltenes and resins and volatiles) can be slightly polar with a dipole moment of less than 1 D.

Acknowledgments

This work was supported by the member companies of the Reservoir Engineering Research Institute (RERI). We thank Dr. O. Mullins and H. Groenzin (Schlumberger-Doll Research Center, CT), Dr. M. Boduszynski and B. Mossberger (Chevron Technology Company, CA), and P. Fotland (Norsk Hydro SA, Bergen) for their help and valuable comments during the course of this work.

Notation

a = molecular radius, m
C = capacitance, $J^{-1} \cdot C^2$
E = electric field, $J \cdot m^{-1} \cdot C^{-1}$
F = internal field, $J \cdot m^{-1} \cdot C^{-1}$
G = cavity field, $J \cdot m^{-1} \cdot C^{-1}$
k = Boltzmann constant, $J \cdot K^{-1}$ ($k = 1.381 \times 10^{-23}$ $J \cdot K^{-1}$)
L = inductance, H
m = total dipole moment, $C \cdot m$
M = molecular weight, $kg \cdot mol^{-1}$
n = refractive index
N = number of molecules per unit volume, $mol \cdot m^{-3}$
N_A = Avogadro number, mol^{-1} ($N_A = 6.022 \times 10^{23}$ mol^{-1})
P = polarization, $C \cdot m^{-2}$
e = electric charge, C
r = distance between charges, m
R = reaction field, $J \cdot m^{-1} \cdot C^{-1}$
R = resistance, Ω
T = temperature, K
u = unit dipole moment
v = volume fraction
w = weight fraction
x = mole fraction

Greek letters

α = polarizability, m^3
ϵ = permittivity, $J^{-1}\cdot C^2\cdot m^{-1}$ ($\epsilon_0 = 8.854\times10^{-12}$ $J^{-1}\cdot C^2\cdot m^{-1}$)
ϵ_r = dielectric constant
ϵ_r' = dielectric storage
ϵ_r'' = dielectric loss
μ = dipole moment, $C\cdot m$
ν = frequency, Hz
ρ = mass density, $kg\cdot m^{-3}$

Subscripts

0 = air/vacuum
1 = nonpolar solvent
2 = polar solute
a = actual
i = component index
ind = induced
M = molar
μ = orientation (or permanent)

Literature Cited

American Society for Testing and Material, Annual Book of ASTM Standards, ASTM D2006, D3279, D893, D2007, D4124, ASTM, Philadelphia, PA (1970, 1978, 1980, 1991a, 1991b).

Andersen, S. I., and J. G. Speight, "Petroleum Resins: Separation, and Role in Petroleum," *Pet. Sci. Technol.*, **19** (1&2) 1 (2001).

Atkins, P. W., *Physical Chemistry*, Oxford University Press, Oxford (1978).

Becker, H. L., "Asphaltene: To Treat or Not," 2000 SPE Permian Basin Oil and Gas Recovery Conf., Midland, TX (2000).

Bitter, F., *Currents, Fields and Particles*, The Technology Press of Massachusetts Institute of Technology and Wiley, New York (1956).

Boduszynski, M., Private Communication, Chevron Technology Company, Richmond, CA (2000).

Born, M., and E. Wolf, *Principles of Optics*, Pergamon Press, New York (1980).

Böttcher, C. J. F., *Theory of Electric Polarization*, Elsevier, Amsterdam (1952).

Buckley, J. S., G. J. Hirasaki, Y. Liu, S. Von Drasek, J.-X. Wang, and B. S. Gill, "Asphaltene Precipitation and Solvent Properties on Crude Oils," *Petroleum Sci. and Technol. Int.*, **16** (3-4), 251 (1998).

Callen, R. B., J. G. Bendoraitis, C. A. Simpson, and S. E. Voltz, "Upgrading Coal Liquids to Gas Turbine Fuels 1. Analytical Characterization of Coal Liquids," *Ind. Eng. Chem. Prod. Res. Dev.*, **15** (4), 223 (1976).

Debye, P., *Polar Molecules*, Dover, New York (1929).

De Hemptinne, J-C., A. Aubertin-Couvreur, I. Fondio, and D. Broseta, "Viscosity Prediction of Heavy Crudes in Hydrotreatment Conditions," Int. Conf. Petroleum Phase Behavior and Fouling, Houston, TX (1999).

Durandeau, M., Private Communication, Total Elf Fina Research Center, Pau, France (1999).

Ese, M.-H., X. Yang, and J. Sjoblom, "Film Forming Properties of Asphaltenes and Resins. A Comparative Langmuir-Blodgett Study of Crude Oils from North Sea, European Continent and Venezuela," *Colloid Polym. Sci.*, **276**, 800 (1998).

Farcasiu, M., "Fractionation and Structural Characterization of Coal Liquids," *Fuel*, **56**, 9 (1977).

Feynman, R. P., R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, Vol. 2, Addison-Wesley, Redwood City, CA (1964).

Firoozabadi, A., *Thermodynamics of Hydrocarbon Reservoirs*, McGraw-Hill, New York (1999).

Groenzin, H., and O. C. Mullins, "Molecular Size and Structure of Asphaltene from Various Sources," *Energy Fuels*, **14** (3), 677 (2000).

Guggenheim, E. A., "The Computation of Electric Dipole Moments," *Trans. Faraday Soc.*, **47**, 573 (1951).

Halverstadt, I. F., and W. D. Kumler, "Solvent Polarization Error and its Elimination in Calculating Dipole Moments," *J. Amer. Chem. Soc.*, **64**, 2988 (1942).

Halvorsen, K., *Dipole Moments and Molecular Weights for Alkane Precipitated Solid Fractions for Some North-Sea Oils*, MSc Thesis, Univ. of Bergen, Institute of Chemistry, Bergen, Norway (1997).

Hewlett-Packard, *The Impedance Measurement Handbook: A Guide to Measurement, Technology and Techniques*, Hewlett-Packard, Hyogo, Japan (1999).

Kaminski, T. J., H. S. Fogler, and A. Mairal, "Classification of Asphaltenes via Fractionation and the Effect of Heteroatom Content on Dissolution Kinetics," Int. Conf. on Petroleum Phase Behavior and Fouling, Houston, TX (1999).

Kumler, W. D., "The Dipole Moment of ms-Tetraphenylporphirine," *J. Amer. Chem. Soc.*, **64**, 2993 (1942).

LeFèvre, R. J. W., *Dipole Moments*, 2nd ed., London (1948).

Leontaritis, K. J., and A. G. Mansoori, "Asphaltene Deposition: A Survey of Field Experience and Research Approaches," *J. Pet. Sci. Eng.*, **1**, 229 (1988).

Lian, H., J. R. Lin, and T. F. Yen, "Peptization Studies of Asphaltene and Solubility Parameter Spectra, *Fuel*, **73**, 423 (1994).

Lide, D. R., and H. P. R. Frederikse, *Handbook of Chemistry and Physics*, 81st ed., CRC Press, Boca Raton, FL (2000).

Maruska, H. P., and B. M. L. Rao, "The Role of Polar Species in the Aggregation of Asphaltenes," *Fuel Sci. Technol. Int.*, **5**(2), 119 (1987).

Maxwell, J. C., *A Treatise on Electricity and Magnetism*, Vol. 2, 3rd ed., Dover, New York (1954).

McClellan, A. L., *Tables of Experimental Dipole Moments*, Vol. 1, Freeman, San Francisco (1963).

McLean, J. D., and P. K. Kilpatrick, "Comparison of Precipitation and Extrography in the Fractionation of Crude Oil Residua," *Energy Fuels*, **11**, 570 (1997).

Mitra-Kirtley, S., O. C. Mullins, J. Van Elp, S. J. George, J. Chen, and S. P. Cramer, "Determination of the Nitrogen Chemical Structures in Petroleum Asphaltenes using XANES Spectroscopy," *J. Amer. Chem. Soc.*, **115**(1), 252 (1993).

Moinelo, S. R., R. M. Menendez, and J. Bermejo, "Fractionation of Coal-Derived Liquids by Extrography," *Fuel*, **67**, 682 (1988).

Murzakov, R. M., S. A. Sabanenkov, and Z. I. Syunyaev, "Influence of Petroleum Resins on Colloidal Stability of Asphaltene-Containing Disperse Systems," *Khim. Tekhnol. Topl. Masel.*, **10**, 40 (1981).

Nalwaya, V., V. Tangtayakom, P. Piumsomboon, and S. Fogler, "Studies on Asphaltenes Through Analysis of Polar Fractions," *Ind. Eng. Chem. Res.*, **38**, 964 (1999).

Newberry, M. E., and K. M. Barker, "Organic Formation Damage Control and Remediation," 2000 SPE Int. Symp. on Formation Damage Control, Lafayette, LA (2000).

Nighswander, J. A., H. Kaira, and A. Majeed, "Effect of Low Molecular Weight Hydrocarbons on the Onset Concentration and Bulk Properties of Asphaltenes at In-Situ Temperature and Pressure Conditions," AIChE Meeting, Houston (1993).

Onsager, L., "Electric Moments of Molecules in Liquids," *J. Amer. Chem. Soc.*, **58**, 1486 (1936).

Oudin, J. L., "Analyse Géochimique de la Matière Organique Extraite des Roches Sédimentaires I. Composés Extractibles au Chloroforme," *Rev. Ins. Fr. Pét.*, **25** (1), 4 (1970).

Pedersen, C., and S. I. Andersen, "Dielectric Properties of Asphaltenes and Oils," AIChE Meeting, Houson, TX (1999).

Pfeiffer, J. Ph., and R. N. J. Saal, "Asphaltic Bitumen as Colloid System," *J. Phys. Chem.*, **44**, 139 (1940).

Riazi, M. R., and T. E. Daubert, "Improved Characterization of Wide Boiling Range Undefined Petroleum Fractions," *Ind. Eng. Chem. Res.*, **26**(3), 629 (1987).

Schabron, J. F., and J. G. Speight, "Solubility and Three-Dimensional Structure of Asphaltenes," *Pet. Sci. Technol.*, **16**(3/4), 361 (1998).

Schwager, I., and T. F. Yen, "Coal Liquefaction Products from Major Demonstration Processes 1. Separation and Analysis," *Fuel*, **57**, 100 (1978).

Sen, A. D., V. G. Anicich, and T. Arakelian, "Dielectric Constant of Liquid Alkanes and Hydrocarbon Mixtures," *J. Phys. D: Appl. Phys.*, **25** (3), 516 (1992).

Smyth, J. W., "Some Developments of Guggenheim's Simplified Procedure for Computing Electric Dipole Moments," *Trans. Faraday Soc.*, **46**, 394 (1950).

Smyth, C. P., *Dielectric Behavior and Structure*, McGraw-Hill, Amsterdam (1955).

Speight, J. G., R. B. Long, and T. D. Trowbridge, "Factors Influencing the Separation of Asphaltenes from Heavy Petroleum Feedstocks," *Fuel*, **63**, 616 (1984).

Speight, J. G., *The Chemistry and Technology of Petroleum*, Marcel Dekker, New York (1999).

Institute of Petroleum, *Standards for Petroleum and its Products*, "IP 143: Asphaltenes Precipitation with Normal Heptane," Institute of Petroleum, London (1957).

Storm, D. A., and E. Y. Sheu, "Characterization of the Asphaltenic Colloidal Particle in Heavy Oil," *Fuel*, **74** (8), 1140 (1995).

Swanson, J. M., "A Contribution to the Physical Chemistry of the Asphalts," *J. Phys. Chem.*, **46**, 141 (1942).

Syncrude, *Syncrude Analytical Method for Oil Sand and Bitumen Processing*, Syncrude Canada Ltd., Edmonton, Alta., Canada (1979).

Van Ness, K., and H. A. Van Westen, *Aspects of the Constitution of Mineral Oils*, Elsevier, Amsterdam (1951).

Waldo, G. S., O. C. Mullins, J. E. Penner-Hahn, and S. P. Cramer, "Determination of the Chemical Environment of Sulphur in Petroleum Asphaltenes by X-ray Absorption Spetroscopy," *Fuel*, **71**, 53 (1992).

Wallace, D., D. Henry, K. Pongar, and D. Zimmerman, "Evaluation of Some Open Column Chromatographic Methods for Separation of Bitumen Components," *Fuel*, **66**, 44 (1987).

Whauquier, J. P., *Crude Oil Petroleum Products Process Flowsheets*, Vol. 1, Technip, Paris (1995).

Wu, J., J. M. Prausnitz, and A. Firoozabadi, "Molecular Thermodynamics of Asphaltene Precipitation in Reservoir Fluids, *AIChE J.*, **46**, 1 (2000).

Manuscript received Dec. 5, 2001, and revision received Mar. 25, 2002.