Asphalt Flocculation and Deposition: I. The Onset of Precipitation

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Formation of asphalt aggregates and their deposition on the pore surfaces of a porous medium, which alter the structure of the medium and its effective properties, is a critical problem to catalytic and oil recovery and refinery processes. Extensive new experimental data for the amount of precipitated asphalt formed with crude oil and various solvents are presented. Results indicate that, contrary to the previous assumptions, asphalt formation is at best partially reversible. A thermodynamic model based on the Flory–Huggins theory of polymer solutions is used, together with the Soave equation of state, to predict the data. Critical evaluation of the model shows that its predictions do not agree well with our data. As an alternative, we propose a new model that employs a scaling equation, somewhat similar to those encountered in aggregation and gelation phenomena. The scaling function takes on a very simple form, and its predictions are in very good agreement with the data. It also predicts that the onset of precipitation may obey a simple universal equation.

Introduction

One of the obstacles in the design and optimization of catalytic coal liquefaction and coal liquid upgrading reactors is the lack of available experimental data for thermodynamic, transport, and reaction properties at realistic process conditions. In these processes one is faced with the task of processing a number of heavy oils, containing metals and other contaminants, in a variety of process-dependent solvents. It is therefore important, on the basis of predicting catalyst activity, selectivity, and optimizing reactor performance, that the thermodynamic, reaction, and transport properties of these oil species be accurately measured or predicted. Over the years, several studies have been undertaken (see, for example, Thrash and Pildes, 1981; Baltus and Anderson, 1983; Sakai et al., 1983; Jost et al., 1985; Mieville et al., 1989; Kyriacou et al., 1988a,b; Nortz et al., 1990; Sane et al., 1988, 1992) in which the transport properties of asphaltenes derived from various types of heavy oil have been measured. Precipitation of the asphaltene aggregates on the pore surfaces of the catalyst causes severe problems for efficient operation of the process.

An important and somewhat related problem in the petroleum industry is deposition of heavy organic compounds on the pore surfaces of oil reservoirs during enhanced oil-recovery processes (Speight, 1991). Miscible displacement of oil by carbon dioxide or natural gas is considered one of the most efficient methods of increasing oil production. However, this process often causes some changes in the fluid flow behavior and the equilibrium properties of the fluids. Under certain conditions such changes can lead to the formation of asphaltenes and asphalts, which are large molecular mixtures with complex structure and properties. Although many authors do not distinguish between asphalt and asphaltene, we define (as do others; see, e.g., Speight, 1991) the former as the latter plus resin, and use this terminology throughout this

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article. Formation of asphalts and asphaltenes is a function of the composition of the crude oil and the displacing agents, and the pressure and temperature of the reservoir. Their deposition on the surface of the pores reduces the permeability of the pore space, leading to the eventual isolation of oil from the flowing fluid in the reservoir (see, for example, Lichaa and Herrera, 1975). The reduction in the permeability reduces the efficiency of oil-recovery processes, and increases significantly their cost. As enhanced oil-recovery processes by miscible displacements have become more popular, formation of heavy organic molecules in the form of asphalt and asphaltene and their deposition on the pore surfaces have gained increasing importance. Deposition of such aggregates on the pore surfaces can also alter the wettability of the reservoir, which is a crucial factor in the distribution of *immiscible* fluids in a porous medium and displacement of oil by an immiscible fluid such as water. Therefore, it is important to understand the mechanisms that give rise to the formation of such aggregates under the reservoir conditions, the point at which the deposition of these molecules on the pore surfaces is triggered, the thermodynamic and transport properties of such molecules, and their effect on the permeability and wettability of the pore space. Although over the past several decades the nature of heavy organic compounds, and in particular asphalt and asphaltene, and the mechanism of their deposition on the pore surfaces of a porous medium have been studied intensively (see, for example, Preckshot et al., 1943; Katz and Beu, 1945; O'Donnell, 1951; Dickie and Yen, 1967; Dickie et al., 1969; David, 1973; Yen, 1974; Koots and Speight, 1975; Monger, 1984; Monger and Khakoo, 1981; Hirschberg, 1984; Hirschberg et al., 1984; Monger and Fu, 1987; Boduszynski, 1987), no general consensus has emerged. One important reason is that these studies were not systematic in that each study considered only one aspect of the problem, and did not investigate the formation and deposition of such compounds, their thermodynamic and transport properties, and their effect on the permeability and wettability of the pore space, all in one study and with similar compounds, and under similar conditions. Moreover, the complexity of the structure of asphalt aggregates has also hindered progress.

Another reason for this lack of consensus is the fact that although asphaltene and asphalt precipitation can, in principle, be experimentally measured, it is not always practical to do so due to the intensive experimental effort that is needed for such measurements. This is particularly true for measurement or prediction of precipitation upon natural gas injection into the reservoir. During this process, the crude oil first comes into contact with the newly injected gas and then with the enriched gas that is the result of earlier contacts. Problems arising from asphalt and asphaltene precipitation have been encountered in many field-scale operations around the world, including those in Algeria (Lihoreau et al., 1967), in the Ventura field in California (Katz and Beu, 1945; Tuttle, 1983), in the production tubing in the Little Creek, Mississippi, during CO_2 injection for enhanced oil recovery (Tuttle, 1983), and in some Iranian oil wells.

The purpose of this article is to present the results of a systematic study of this phenomenon. We are particularly interested in the formation and deposition of asphalt and asphaltene aggregates under the operating conditions of an oil reservoir. However, as these phenomena are not even well-understood at atmospheric pressure, in the present article we focus our attention on the behavior of the system, under atmospheric pressure, near the onset of precipitation that is particularly important to oil recovery, present new experimental data, and discuss two theoretical approaches for predicting them. One of these approaches was developed previously by others, while the other one is proposed by us. Previously, limited data of the type we present here were given by Mitchell and Speight (1973), Hotier and Robin (1983), Hirschberg et al. (1984), and Speight et al. (1985). In sequels to this article we shall study the kinetic growth of asphalt and asphaltene aggregates, their phase behavior in immiscible and miscible displacements and at elevated temperatures and pressures, and their flow and its effect on the permeability of a porous medium. Their transport properties, such as their effective diffusivity in a pore, have been reported elsewhere (Ravi-Kumar et al., 1994).

The plan of this article is as follows. In the next section we describe the experimental procedures for measuring the quantities of interest. This is then followed by the presentation and discussion of the experimental results. We then present two theoretical approaches for predicting the data. The article is summarized and discussed in the last section.

Experimental Procedure

Tank oil analysis

The crude oil under study was a light tank oil with an API° 29.7. It was obtained from an oil field in southwest Iran. Table 1 shows its chemical composition and PVT properties. We did not analyze the elemental composition of the crude oil, as it is not crucial to our discussion in this article. The tank oil was filtered so as to remove its solid contents, such as sand. After any experiment, the asphaltene content of the tank oil was measured by the standard IP-143 procedure, and also by the thin layer chromatography method. This method has been used in the past for measuring the asphaltene constents of natural bitumens and residual oil. We modified and adopted this method for measuring the asphaltene content of light oil. As we used this method extensively for measuring the experimental data that will be presented in Part II of this article, where we present and discuss our results for the kinetic growth of asphaltene and asphalt molecules, we defer the details of this method and refer the reader to that article. The asphaltene content of the tank oil was about 2.2 weight percent, and that of asphalt was about 11%.

Table 1. Tank Oil PVT Data

Component	mol %	Component	mol %
C_1	0.0	i-C_5	1.69
C_2	0.0	n-C_5	2.21
C_3	0.0	n-C_6	4.23
i-C_4	0.05	C_7^+	91.18
n-C_4	0.64		

C_3-asphalt wt. % = 11; n-C_7-asphalt wt. % = 2.2; molecular weight of the oil (measured by vapor pressure osmometer) = 200; specific gravity of the oil (at 60/60°F) = 0.8778 g/cm^3; wt. % of C_{33}^+ fractions = 12.66; specific gravity of C_{33}^+ fractions (at 60/60°F) = 1.0186 gr/cm^3; normal boiling point of C_{33}^+ fractions = 468°C.

Measurement of the onset and amount of asphalt precipitation

In order to precipitate the asphalt, the tank oil was first diluted by the addition of a solvent (diluent). The solvent that we used was a normal alkane with a carbon number ranging from 5 to 10. Several different dilution ratios, *R*, measured in terms of the cm^3 of the solvent/g of the oil, were also used. The diluted oil was then agitated for some time, during which it precipitated asphalt sludge, which after one day was filtered by a No. 42 Wattman paper filter. Then, the same solvent was used to wash the tank oil that had remained in the asphalt on the paper filter. The amount of the asphalt on the filter paper was then measured by dissolving it in another solvent, which in this case was toluene. The solvent was then evaporated in an oven at a temperature between 100 and 110°C. The remaining solid deposit was asphalt that was weighed by an accurate analytical balance, and the results were recorded on the basis of the weight percent, *W*, of the tank oil. During the entire experiment the laboratory temperature was kept at 26 ± 2°C.

Reversibility

An important issue is whether precipitation of asphalt is a reversible process. This has been a controversial issue for several years and, because of lack of precise experimental data, it has remained unresolved. Several parameters affect precipitation of asphalt and asphaltene, each one of which influences it differently. For example, if asphalt formation and precipitation is due to elevation of the pressure, then the process is generally thought to be reversible. However, temperature and compositions of the crude oil and the solvent have much stronger influence on this process, and therefore formation and precipitation of asphaltene and asphalt due to a change in the temperature or composition could be at least partially irreversible. The issue of reversibility is also crucial to the validity of classic thermodynamic models for predicting the experimental data presented in this article since, in principle, only if this phenomenon is reversible, can one use such models. Up to now, there has been no firm indication for complete irreversibility of this phenomenon, since adding a solvent is not the reverse process of adding a precipitant.

To study this issue, two sets of experiments were conducted at atmospheric pressure. In the first set of experiments asphalt precipitation was triggered by the addition of normal hexane as the solvent at a solvent-to-crude ratio $R = 3$ cm^3/g. The solvent and the crude oil were mixed by uniform shaking of the tube. This mixing did not affect the results. The amount of deposition was then measured. Then, the solvent was stripped so that the composition of the mixture was close to that of the initial composition of the tank oil, and the amount of the precipitated asphalt was measured again. The second set of experiments was conducted by addition of fresh oil (instead of stripping the solvent) in order to decrease the solvent-to-crude ratio and make it close to the critical ratio R_c for the onset of asphalt precipitation for the tank oil and normal heptane as its solvent. The amount of the precipitated asphalt was then measured under the new conditions, and was compared with that obtained in the first set of experiments. To check the precision of the data the measurements were carried out twice.

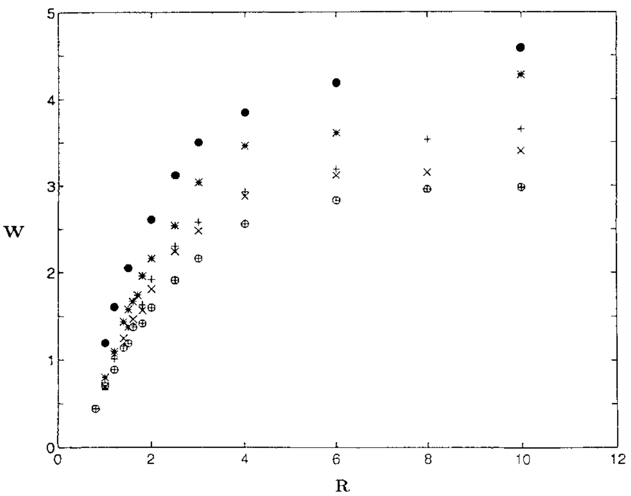

Figure 1. Experimental data for the weight percent *W* of precipitated asphalt as a function of the solvent to crude oil ratio *R* (in cm^3/g).

Results are from top to bottom for n-C_5, n-C_6, n-C_7, n-C_8, and n-C_{10} as the solvent.

Experimental Results and Discussion

Figure 1 shows our experimental results for the weight percent of precipitated asphalt *W*, in weight of the asphalt/g of the crude oil, for five different solvents (n-alkanes) and various solvent-to-crude ratios *R*. Our data are consistent with the previous results mentioned earlier. For example, Hirschberg et al. (1984) have presented very limited data for n-C_5, n-C_7, and n-C_{10} at only three different values of *R*. The trend of their data for these values of *R* is consistent with ours, although a numerical comparison between their data and ours is not possible, because they do not specify the temperature of their experiments. Since the addition of a solvent does not always guarantee precipitate formation, the onset of asphalt precipitation for each solvent, that is, the critical ratio R_c at which precipitation starts for the first time, can be estimated by extrapolating the results to $W = 0$. However, this extrapolation can be inaccurate, as the experimental data close to this point are very difficult to measure, and can be subject to uncertainties. In general, R_c is expected to be a function of the compositions of the oil and the solvent, and the temperature. We will return to prediction of R_c later in this article.

The results of the reversibility study for the first set of the experiments discussed previously, in which hexane was used as the solvent, are shown in Table 2. In these experiments the tank oil was held at 60°C (near the boiling point of hexane, the solvent) to ensure that there was no change in its chemical composition and weight. Several experiments were

Table 2. Dissolution of Precipitated Asphalt by Stripping of Solvent and the Resulting wt. % *W* of Asphalt*

Immediately after Mixing	2 h after Mixing	60 h after Mixing
2.679	2.450	0.180
2.690	2.352	0.726
2.684	2.410	0.752

*The first two lines of the table give the results for the first and second runs, and the third line is the average of the two runs.

Table 3. Dissolution of Precipitated Asphalt by Addition of Fresh Oil, and the Resulting wt. % W of Asphalt*

R	Contact Time (h)	R (After Addition of Oil)	W (Asphalt)
3.475	2	3.475	2.958
3.475	2	3.475	2.888
3.475	24	0.688	1.112
3.475	24	0.688	1.125

*The four rows give the results for four different experiments. The ratio R on the left is the solvent-to-tank-oil ratio, while the R on the right is for solvent-to-tank-oil ratio after addition of oil (see the text). The oil was added after 2 h, and therefore the first two rows do not show any change.

conducted to study the effect of mixing time. A series of experiments was carried out for the asphalt content immediately after the addition of the solvent. The second series was conducted 2 hours after the addition of the solvent, and the last series after 60 hours. The results shown in Table 2 show 72% reduction in the amount of the precipitated asphalt after removal of the solvent and the subsequent change in the composition of the mixture to that of the original tank oil. Therefore, these results suggest that the process is at best *partially* reversible.

The results of the second set of experiments, in which fresh oil was used to change the composition of the mixture (see above), are presented in Table 3. In this set of experiments, normal heptane was added to the tank oil at a ratio $R = 3.5$ cm^3 of the solvent/g of the tank oil. Some of the samples were measured for asphalt deposition after 2 hours. Fresh tank oil was added to other samples after 2 hours in order to decrease the solvent-to-crude ratio R to a value close to the critical value R_c for the onset of precipitation. The new solvent-to-crude ratio was $R = 0.69$ cm^3/g. The amount of the precipitated asphalt in the samples to which fresh oil was added was measured after 24 hours. During these experiments, the temperature of the samples was held at 14±2°C, and the samples were occasionally agitated for a period of 30 seconds. It is important to point out that in our experiments the amount of precipitated asphalt and asphaltene were the same after 2 and 24 hours after the mixing of the oil and the solvent. The results shown in Table 3 indicate 62% reduction in the amount of the precipitated asphalt after 24 hours, confirming that this phenomenon is at best partially reversible.

Theoretical Modeling

Any crude oil is a complex mixture of various hydrocarbons and some elements such as nitrogen, oxygen, and sulfur. This complex mixture is usually in a delicate equilibrium, which can be distorted by a change in the temperature, pressure, or composition. The distortion results in asphalt precipitation. After some time an equilibrium is reached again, and precipitation essentially stops. Because of this delicate balance, predicting the onset of precipitation and other properties is a difficult problem that has not yet found a satisfactory solution. In this section we present two theoretical approaches for predicting our experimental data. One is a thermodynamic model, based on the assumption that the precipitation process is a reversible phenomenon. Since our results discussed earlier already indicated that this phenomenon is at best partially reversible, we expect this approach not to be a completely satisfactory method of predicting the data. However, this approach is relatively simple and is currently used in the oil industry. One of our major goals for using this approach is evaluating it critically, and testing its accuracy for predicting our data. Another goal is to explain clearly the assumptions and approximations that are made in order to develop this model, since this has not been done clearly in the literature. Finally, we would like to make a direct comparison between the performance of this approach and that of the model that we propose in this article. The second approach that we propose in this article uses the analogy between asphalt formation and aggregation and gelation phenomena, and builds on the universal properties that such phenomena possess. What follows is a detailed description of each approach.

Thermodynamic Model

According to Long (1981) asphalts are highly dispersed and polymerlike molecules that contain a broad distribution of various groups in their structure. Because of their similarity with polymers, an attempt has been made to use the Flory–Huggins theory of polymer solutions (Flory, 1944; Huggins, 1942) for predicting the onset of asphalt precipitation. Hirschberg et al. (1984) were the first to propose this approach. They assumed that the crude oil is a homogeneous binary mixture of asphalt and the solvent, and that the precipitated asphalt is a homogeneous solid compound. In reality neither assumption is completely true, as neither is the crude oil a homogeneous mixture, nor is the precipitated asphalt a single solid. However, the approach of Hirschberg et al. is relatively simple (see below). Kawanaka et al. (1991) modified this approach using the statistical mechanical theory of Scott and Magat (1945) for heterogeneous polymer solutions. Briefly, this theory, which is based on Huggins' theory, incorporates a molecular weight distribution in order to take into account the heterogeneity of the polymer solution. Kawanaka et al. (1991) assumed that asphalt consists of many components of similar polymeric molecules so that a continuous molecular weight distribution, which they assumed to be a gamma distribution, can be used. However, in the absence of extensive and accurate experimental data for the molecular weight distribution of asphalts and asphaltenes (Moschopedis et al., 1976), we think it is premature to use this approach. Thus, in this article we use the original method of Hirschberg et al. (1984) for predicting our experimental data, and comment on the results of Kawanaka et al. (1991).

The Flory–Huggins theory studies the equilibrium between a polymer and a solvent, and predicts the solubility of the polymer in the solvent. According to this theory the chemical potential μ_p of the polymer at temperature T is given by

$$\mu_p - \mu_0 = R_g T\left[\ln \phi_p + \left(1 - \frac{V_p}{V_s}\right)\phi_s\right] + V_p(\delta_p - \delta_s)^2 \phi_s^2, \quad (1)$$

where ϕ_p and ϕ_s are, respectively, the volume fraction of the polymer and the solvent, V_p and V_s are their respective molar volume, δ_p and δ_s are their solubility parameter, R_g is the gas constant, and μ_0 is a reference chemical potential. The solubility parameter δ is usually predicted by using the Hildebrand equation

$$\delta = \left(\frac{\Delta H - R_g T}{V} \right)^{1/2}, \tag{2}$$

where ΔH is the heat of vaporization, and V is the molar volume. To use this theory one assumes that asphalt can be represented as a polymer, that the crude oil is the solvent, and that asphalt precipitation is a reversible process. We denote the asphalt and the solvent by subscripts a and s, and the liquid and solid phases by superscripts L and S, respectively. At equilibrium, the chemical potentials of the asphalt in the liquid and solid phases must be equal, $\mu_p^L = \mu_p^S$. Then the equality of the chemical potentials, together with Eq. 1, yield the following equation for the volume fraction ϕ_a^L of the asphalt in the liquid phase

$$\phi_a^L = \phi_a^S \exp\left[\phi_s^L \left(\frac{V_a^L}{V_s^L} - 1 \right) - \frac{V_a^L (\phi_s^L)^2}{R_g T} (\delta_a - \delta_s)^2 \right]. \tag{3}$$

If we now define

$$\delta_L = \phi_a^L \delta_a + \phi_s^L \delta_s, \tag{4}$$

then it follows that

$$(\delta_a - \delta_s)^2 (\phi_s^L)^2 = (\delta_a - \delta_L)^2. \tag{5}$$

Let V^L be the molar volume of the crude oil–asphalt liquid mixture. Then

$$V^L = x_a V_a^L + x_s V_s^L, \tag{6}$$

where $x_a(x_s)$ is the mole fraction of the asphalt (solvent). Since $\phi_s^L = x_s V_s^L / V^L$, we obtain

$$\phi_s^L \left(\frac{V_a^L}{V_s^L} - 1 \right) = \frac{V_a^L}{V^L} - 1. \tag{7}$$

Therefore, Eq. 3 is simplified to

$$\phi_a^L = \phi_a^S \exp\left[\frac{V_a^L}{V^L} - 1 - \frac{V_a^L}{R_g T} (\delta_a - \delta_L)^2 \right]. \tag{8}$$

If the solid phase is pure asphalt (or asphaltene), then $\phi_a^S = 1$ and Eq. 8 predicts the maximum amount of asphalt (or asphaltene) that is soluble in the crude oil. Therefore, the difference between the maximum amount (in weight percent) of asphalt or asphaltene W_m that is measured in an experiment and what is predicted by Eq. 8 yields the amount of the precipitated solid. In the past W_m was taken (Hirschberg et al., 1984; Kawanaka et al., 1991) to be the maximum amount of asphalt that is caused by propane, which is usually about 10–12%, although it can be as large as 18%. The idea is that among all solvents propane can generate the maximum amount of asphalt or asphaltene, and in fact injection of C_3 is a standard method of removal of asphalt and asphaltene in many oil refinery operations. However, propane cannot cause any precipitation at atmospheric pressure, the pressure at which our data presented in this article, and those of others mentioned earlier, were measured (for data at higher pressures see Part II of our article). Therefore, this practice is in some sense inconsistent. On the other hand, for any given solvent, one can easily find W_m from the experimental data, since this quantity is that value of W at which the $W-R$ curves saturate and become more or less horizontal (see Figure 1). However, if we use such a W_m, instead of that of propane, the predictions of the thermodynamic model presented below will be grossly in error.

Thus, the procedure to predict the amount of precipitation is as follows. An equation of state is used to predict the liquid molar volume V^L of the crude-oil–asphalt mixture and the heat of vaporization ΔH, from which the solubility parameter δ_L is calculated (using Eq. 2). This involves several assumptions and approximations, as the crude oil is a multicomponent mixture of many compounds, so that either one has to do a phase equilibria calculation involving a large number of components, a difficult task, or represent the crude oil by one or a few pseudo-components, which may or may not be an accurate representation of the mixture. Experimental studies of Mitchell and Speight (1973), Hirschberg et al. (1984), and others indicate that the solubility parameter δ_a of asphalt is close to that of naphthalene, and that the molar volume V_a^L of asphalt in the liquid phase varies between 1 and 4 m^3/kmol. Thus, one can either treat V_a^L as an adjustable parameter, or else fix it at some reasonable value and carry out the computations. Since the results are not very sensitive to V_a^L, this quantity can be fixed without great error. However, in our calculations we treated both V_a^L and δ_a as adjustable parameters. Once the four parameters V^L, V_a^L, δ_a, and δ_L have been determined, Eq. 8 is used to predict ϕ_a^L, from which the amount of the precipitated asphalt (in weight percent) is calculated from $W = W_m - \phi_a^L$.

In this article we use the Soave equation of state (Soave, 1972), which is given by

$$P = \frac{R_g T}{V - b} - \frac{a}{V(V+b)}, \tag{9}$$

where V is the molar volume, P is the pressure, and a and b are two coefficients of the equation that, for a multicomponent mixture, are given by

$$a = \sum_\alpha \sum_\beta x_\alpha x_\beta a_{\alpha\beta}, \tag{10}$$

$$a_{\alpha\beta} = (1 - k_{\alpha\beta}) \sqrt{a_\alpha a_\beta}, \tag{11}$$

$$b = \sum_\alpha x_\alpha b_\alpha. \tag{12}$$

The pure component parameters a_α and b_α are given by

$$a_\alpha = 0.42747 \frac{R_g^2 T_{c\alpha}^2}{P_{c\alpha}} \gamma, \tag{13}$$

$$b_\alpha = 0.08664 \frac{R_g T_{c\alpha}}{P_{c\alpha}}, \tag{14}$$

with

$$\gamma = \left[1 + A\left(1 - \sqrt{T_{r\alpha}}\right)\right]^2, \tag{15}$$

$$A = 0.48 + 1.547\omega_\alpha - 0.176\omega_\alpha^2. \tag{16}$$

Here $T_{c\alpha}$, $P_{c\alpha}$, and ω_α are the critical temperature, pressure, and acentric factor of component α, respectively, and $T_{r\alpha} = T/T_{c\alpha}$. The interaction parameter $k_{\alpha\beta}$ is usually fitted to some experimental data. We also carried out some computations with the Peng–Robinson equation of state (Peng and Robinson, 1976), and found the results to be in close agreement with those obtained with the Soave equation. The heat of vaporization is predicted by the Soave equation to be

$$\Delta H = \left(\frac{a}{b} - \frac{T}{b}\frac{da}{dT}\right)\ln\left(1 + \frac{b}{V}\right). \tag{17}$$

The heat of vaporizations that are predicted by Eq. 17 are usually highly accurate, whereas the predicted molar volumes are usually 10–20% too large.

The first step in the calculations is to fit the interaction parameter $k_{\alpha\beta}$ to the experimental data for the crude oil and solvents used in this study. To do this, one can carry out a standard liquid–vapor equilibria calculation and adjust $k_{\alpha\beta}$ in such a way that the predictions match the data as closely as possible. This requires vapor–liquid equilibria data, for example, the mole fractions of various components of the mixtures in both phases. Thus, the crude oil used in our study was analyzed in the laboratory of the National Iranian Oil Company (see Table 1). The mixture was passed through three different separators at three different pressures and temperatures, which led to flash vaporization and vapor–liquid equilibria. The compositions of the mixtures in both phases were analyzed in a gas chromatographic column, and the mole fraction of each component was determined. We then used the standard practice of assuming that all the C_7^+ components in the mixture can be represented by a single pseudocomponent. To use the Soave equation (or any other equation of state for that matter), the critical properties of the pseudocomponent, its $T_{c\alpha}$ and $P_{c\alpha}$, and its acentric factor ω_α, have to be determined. In the literature there are many empirical or semiempirical correlations for determining such properties for C_7^+ fractions (for a review, see Whitson, 1984). For most of such correlations, the input parameters are the molecular weight M, the normal boiling point T_b, and the density ρ of the C_7^+ fractions. The molecular weight of the mixture can be determined by vapor pressure osmometry, which was also used in this study. The molecular weight of the crude oil was found to be about 200. Whitson (1984) provides empirical graphs for estimating T_b and ρ of the C_7^+ mixtures, if their molecular weight is known. To the best of our knowledge, his graphs and correlations, though empirical or semiempirical, are highly accurate, and thus we used these graphs in our calculations. Given these properties, the acentric factor of the C_7^+ fractions was estimated from the following empirical correlation given by Whitson (1984)

$$\omega_\alpha = -1 + 0.042K + 0.00218T_b, \tag{18}$$

where K is given by

$$K = 91.27\left(\frac{M}{g}\right)^{0.496} T_b^{-0.756}, \tag{19}$$

in which g is the specific gravity. The specific gravity of the crude was 0.8778 g/cm^3 (at 60/60°F).

Having determined the critical properties and the acentric factor of the pseudocomponent C_7^+, two-component liquid–vapor equilibria calculations were carried out using the Soave equation, and the interaction parameter $k_{\alpha\beta}$ was varied until the predicted mole fractions in both phases matched the data as closely as possible. The results for the interaction parameter of various binary mixtures are presented in Table 4. It is seen that the interaction parameter is independent of the temperature and pressure of the system. Using these values of $k_{\alpha\beta}$, the molar volume V^L was calculated for various solvents and solvent-to-crude-oil ratios R. The results are presented in Figure 2. As can be seen, this quantity is not very sensitive to R, and varies little as R is changed by about one order of magnitude. With the aid of Eq. 17, the heat of vaporization ΔH was also calculated, from which the solubil-

Table 4. Interaction Parameter $k_{\alpha\beta}$ of the Soave Equation for Various Binaries*

$k_{\alpha\beta}$	First Separator	Second Separator	Third Separator
$(i\text{-}C_4)\text{-}C_7^+$	0.05	0.05	0.05
$(n\text{-}C_4)\text{-}C_7^+$	0.04	0.04	0.04
$(i\text{-}C_5)\text{-}C_7^+$	0.00	0.00	0.00
$(n\text{-}C_5)\text{-}C_7^+$	0.00	0.00	0.00
$(n\text{-}C_6)\text{-}C_7^+$	0.00	0.00	0.00

*The results were obtained from the fit of the experimental vapor–liquid data in the three separators. The first separator operated at 8.2 atm and 37.8°C, the second one at 1.72 atm and 32.2°C, and the third one at 1.58 atm and 21.1°C.

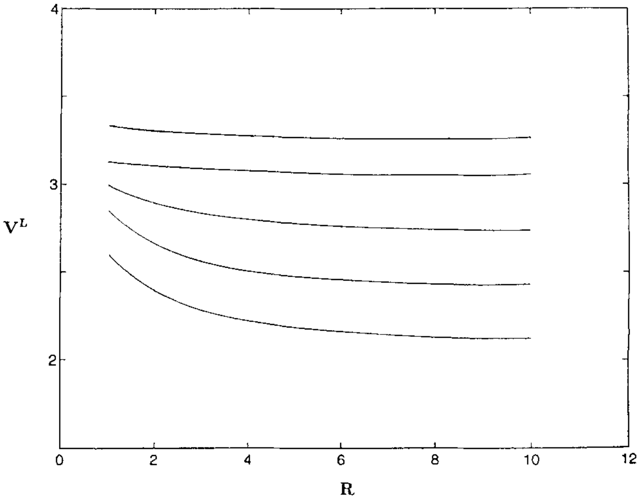

Figure 2. Calculated molar volume V^L (in ft^3/mol) of the liquid phase as a function of the solvent to crude oil ratio R.

Results are from bottom to top for n-C_5, n-C_6, n-C_7, n-C_8, and n-C_{10} as the solvent.

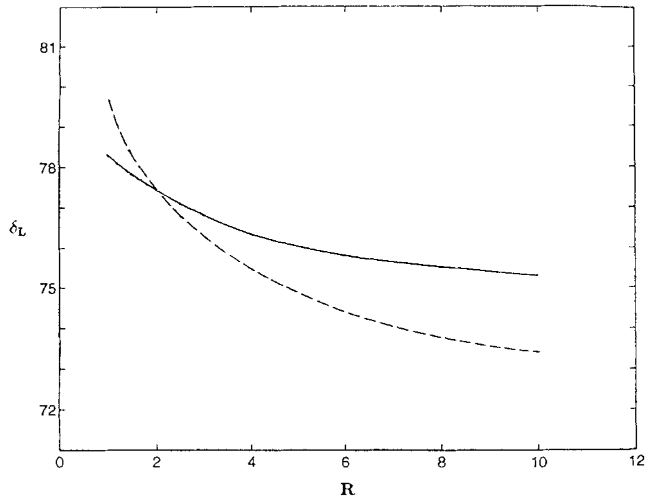

Figure 3. Calculated solubility parameter δ_L [in (Btu/ft^3)$^{1/2}$] of the liquid phase as a function of the solvent to crude oil ratio *R*.

- - - -, n-C_5 as the solvent; —, n-C_{10} as the solvent.

ity parameter δ_L was estimated using Eq. 2. The results are shown in Figure 3. Equation 8 (with $\phi_a^S = 1$) was then used for predicting ϕ_a^L, in which the molar volume V_a^L and the solubility parameter δ_a of asphalt were treated as adjustable parameters.

The results are shown in Figures 4–8, where they are compared with our experimental data and the predictions of the scaling equation to be discussed below. The predictions for the C_5 case are not accurate, while those for the C_6 case are reasonable. In the case of C_7 the predictions are poor, except near the onset of precipitation, while for the C_8 and C_{10} cases the predictions and the data differ greatly. Thus, as can be seen, in no case are the predictions in close agreement with the data for all values of R. As mentioned before, to improve this model Kawanaka et al. (1991) represented the asphalt as a continuous mixture of many components, and used a molecular weight distribution to represent it. They carried out calculations similar to ours, and predicted the $W-R$ curves for C_5, C_7, and C_{10}. For each case, they compared their predictions with three data points given by Hirschberg et al. (1984). While their predictions for the C_{10} case were in reasonable agreement with the data, no significant improvement was obtained for C_5 and C_7 cases, and in fact their predictions for the C_7 case were even poorer than our predictions. One reason for the poor performance of this model is the fact that, as our experiments discussed earlier indicate, asphalt formation is not a reversible process, whereas the fundamental assumption behind the thermodynamic model is the complete reversibility of this phenomenon. Another reason is the many assumptions and approximations that are made in order to arrive at a tractable model. Some of these approximations are uncontrolled, while some of the assump-

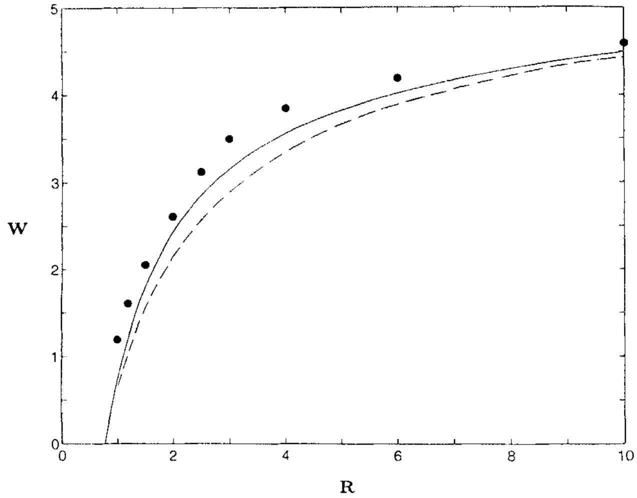

Figure 4. Experimental data (●) for the wt. % *W* of precipitated asphalt vs. predictions of the thermodynamic model (- - - -) and scaling equation (Eq. 21) (—), with n-C_5 as the solvent; *R* is the solvent-to-crude-oil ratio.

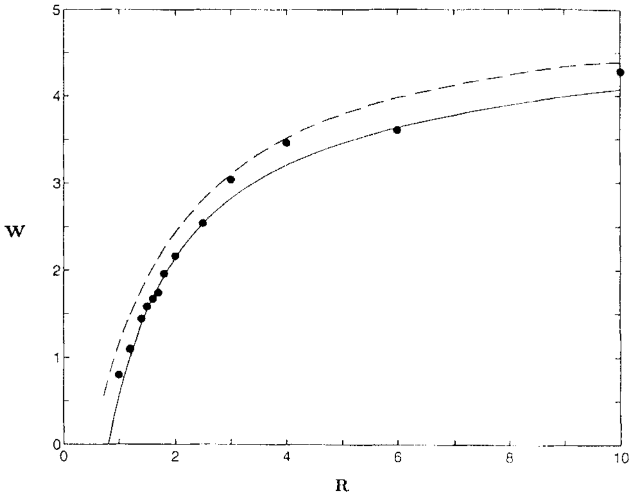

Figure 5. Same as in Figure 4, but with n-C_6 as the solvent.

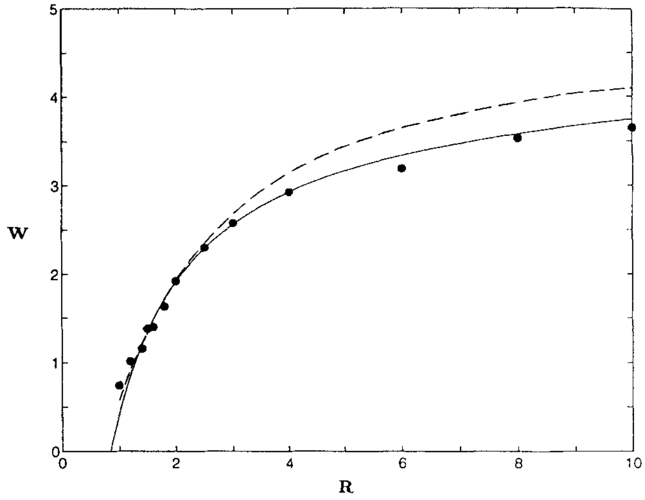

Figure 6. Same as in Figure 4, but with n-C_7 as the solvent.

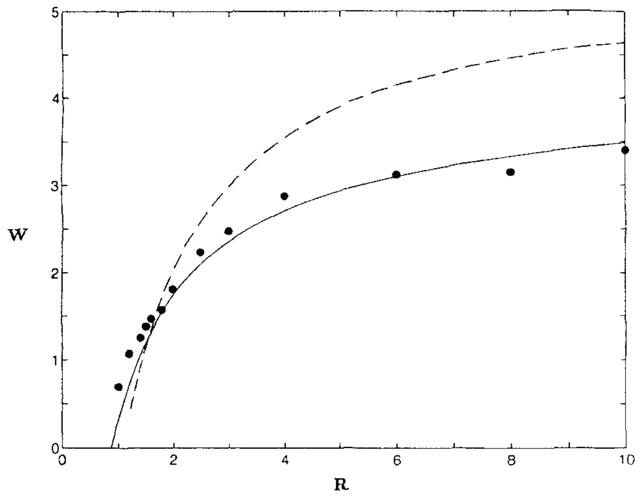

Figure 7. Same as in Figure 4, but with n-C_8 as the solvent.

tions are unjustified. For example, one might improve the predictions by treating the C_7^+ fractions not as just one pseudocomponent, but as at least a few. However, experience with such a modeling (Whitson, 1984) indicates that the results will not be dramatically more accurate than what we presented here with just one pseudocomponent. We may conclude that the thermodynamic model in its current form is not a reliable tool for predicting the amount of precipitated asphalt.

Scaling Equation of State

Our experimental data presented in Figure 1 are strongly suggestive of the possibility that a scaling equation may be developed for predicting them. All the curves in Figure 1 start at about the same point (close to their onset of precipitation), and at large values of R they become more or less parallel. Formation of large asphalt or asphaltene structures is to some extent similar to aggregation and gelation phenomena (Park and Mansoori, 1988), which possess universal properties, independent of many microscopic properties of their structure. In particular, the structural and physical properties of aggregates and gels obey universal scaling equations (for a review of aggregation phenomena, see Meakin, 1988, for a review of gelation processes and their modeling, see Sahimi, 1992, 1994). How the formation of asphalt and asphaltene is related to aggregation and gelation phenomena will be discussed in Part II of this series, but for now we use the analogy between asphalt and asphaltene formation and these phenomena and develop a scaling equation for predicting our experimental data.

The three variables of the data shown in Figure 1 are W, the weight percent of the precipitated asphalt, R, the ratio of the volume of the injected solvent and the weight of the crude oil, and M, the molecular weight of the solvent. Thus, we hypothesize that, similar to aggregation and gelation phenomena, all the data shown in Figure 1 can be collapsed onto a single curve, known as the *master curve* among polymer researchers, and as the *scaling function* in statistical physics, if we combine the three variables into two by taking $X = R/M^z$ and $Y = W/R^{z'}$. Indeed, if we choose

$$z = \frac{1}{4}, \qquad z' = -2, \tag{20}$$

the data collapse onto a single curve, as shown in Figure 9. As can be seen, the data collapse is good but not complete, which is because of the uncertainties and fluctuations in the data, and also due to the fact that the onset of precipitation is not the same for all the solvents. However, we could not find any other values for z and z' that could collapse the data onto a single curve with the same accuracy, nor could we find any other combinations of the three variables that collapse the data onto a single curve. Thus these combinations of the variables and the values of z and z' appear to be unique. For $X > X_c$, where X_c is the value of X at the onset of precipitation, the scaling function can be represented very accurately by a third-order polynomial given by

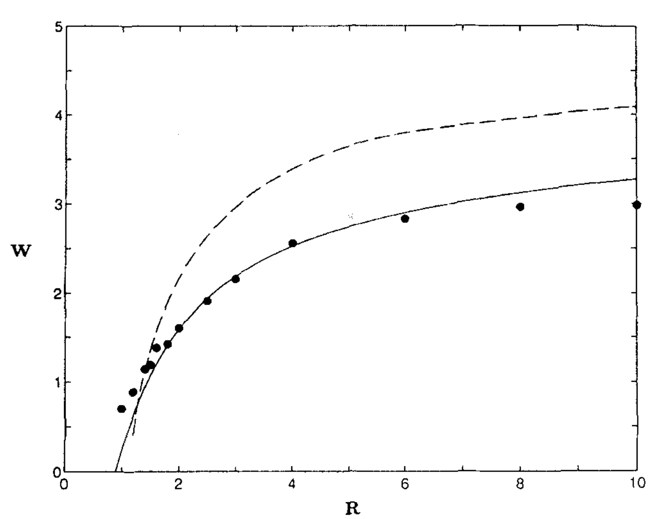

Figure 8. Same as in Figure 4, but with n-C_{10} as the solvent.

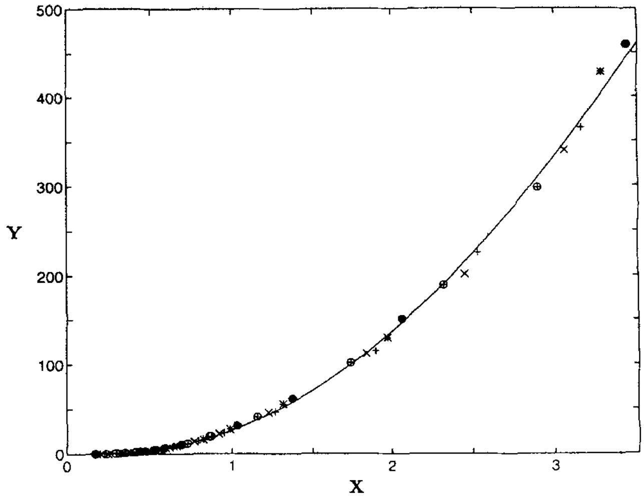

Figure 9. Scaling equation (Eq. 21) with $X = R/M^{1/4}$ and $Y = WR^2$.

Symbols represent the rescaled experimental data.

$$Y = 1.18 - 14.9X + 39.16X^2 + 0.92X^3, \qquad (21)$$

also shown in Figure 9. Equation 21 is obtained by fitting the collapsed data to the polynomial. Higher- or lower-order polynomials do not provide as accurate a fit as Eq. 21, and therefore we believe that this equation is a highly accurate representation of our experimental data. Since the data can be collapsed onto a single curve, the universal scaling curve or its approximation by Eq. 21 can be used to back calculate the experimental data shown in Figure 1. Figures 4–8 show the results of such calculations, where they are also compared with the predictions of the thermodynamic model, and as can be seen, the predictions of the scaling function are in very good agreement with the data. The difference between these predictions and the data in all cases is no more than 10%, comparable to the accuracy of the experimental data, whereas the predictions of the thermodynamic model are generally not in good agreement with the data.

It may be argued that since we have used all the data to arrive at the scaling curve, it is not surprising that the predictions and the data are in very good agreement. However, the collapse of the data onto a single curve has three important implications and consequences. First of all, the possibility that such data can be collapsed onto a single curve is novel and surprising, since usually dimensionless groups can collapse the data onto a single curve, whereas our X and Y are not dimensionless. Secondly, such a scaling curve also provides accurate predictions for those values of R for which no data are available, or their measurement may be difficult. Finally, the scaling representation of the data implies a universal property for the *onset of precipitation*, to be discussed below. But, to show that the data collapse is robust, and that a scaling function can be obtained from far fewer data points with comparable accuracy, and to also get some idea about the effect of fluctuations and uncertainties in the data on their collapse, we also collapsed onto a single curve only the data for n-C_5 and n-C_6, the lightest solvents used in our experiments, and again found that the same z and z' collapse the data. The resulting scaling function is shown in Figure 10. For $X > X_c$, the scaling curve is represented by

$$Y = 0.54 - 12.66X + 38.77X^2 + 1.24X^3. \qquad (22)$$

Note the closeness of the coefficients of Eq. 22 to those of Eq. 21. We then used Eq. 22 to predict the experimental data for n-C_7, n-C_8, and n-C_{10}. The results are shown in Figures 11–13, and it is seen that the accuracy of the predictions is comparable with those shown in Figures 6–8. We also collapsed the data for n-C_8 and n-C_{10}, the heaviest solvents used in our experiments, and found again that the same z and z' cause the data collapse onto a single curve. The resulting scaling function is shown in Figure 14. For $X > X_c$ the scaling function is described by

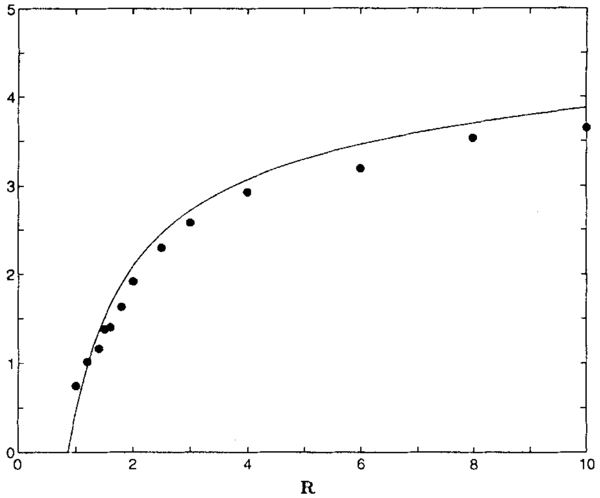

Figure 11. Experimental data (●) for the wt. % W of precipitated asphalt vs. predictions of scaling equation (Eq. 22), with n-C_7 as the solvent; R is the solvent-to-crude-oil ratio.

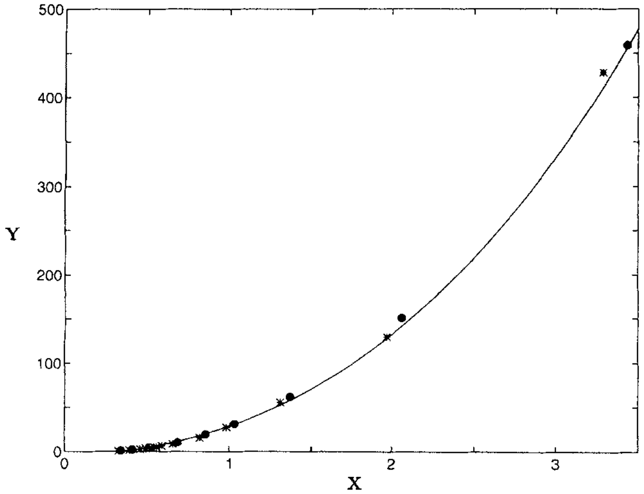

Figure 10. Scaling equation (Eq. 22) with $X = R/M^{1/4}$ and $Y = WR^2$.

Symbols represent the rescaled experimental data for n-C_5 and n-C_6.

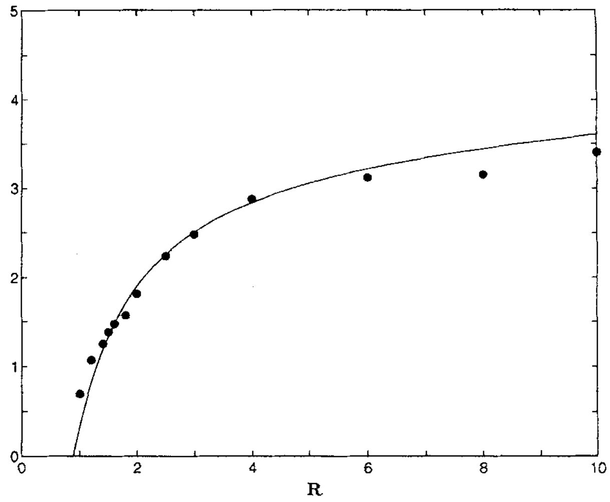

Figure 12. Same as in Figure 11, but with n-C_8 as the solvent.

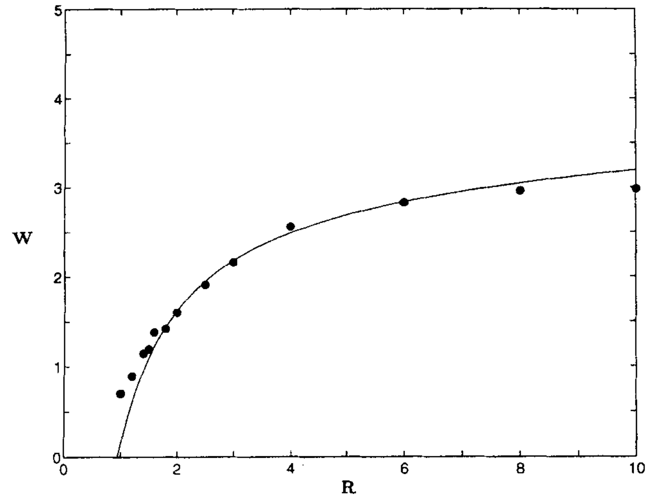

Figure 13. Same as in Figure 11, but with n-C$_{10}$ as the solvent.

$$Y = -0.76 - 8X + 36.27X^2 + 0.8X^3. \qquad (23)$$

Although the coefficients of the linear terms are now somewhat different from those of Eq. 21, the dominant second- and third-order terms are still similar to those of Eq. 21, and in fact there is only a small difference between the predictions of the three equations, which is entirely due to the uncertainties in the data. Equation 23 was then used to predict the data for n-C$_5$, n-C$_6$, and n-C$_7$. The results are shown in Figures 15–17, and as expected the accuracy of the predictions is comparable with the other cases. In fact, the collapse of *any* two sets of data provides reasonably accurate predictions for all other data, that is, *with a limited amount of experimental data, one can make accurate predictions for other systems for which data are not available.* Moreover, as Figures 11–13 and 15–17 demonstrate, the data for light solvents can be used for accurate predictions for heavy solvents, and vice versa. Finally, using Eq. 21, we predicted the precipitate weight percent W as a function of R for the normal alkanes for which no data are available. The results for n-C$_9$, n-C$_{11}$, n-C$_{12}$, and n-C$_{13}$, or more precisely for solvents that have the same molecular weights as these alkanes, are shown in Figure 18.

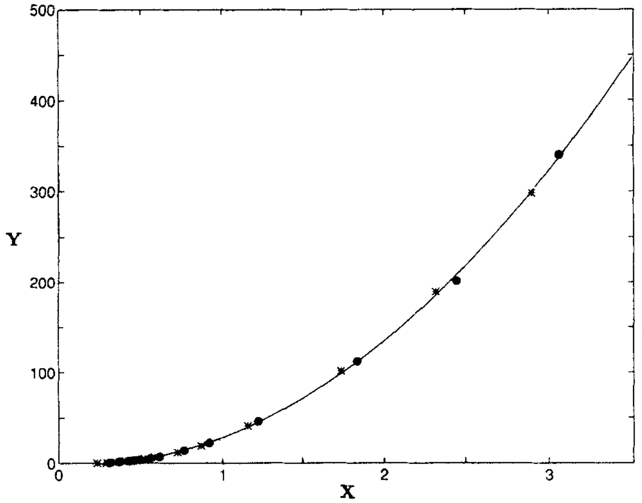

Figure 14. Scaling Eq. 23 with $X = R/M^{1/4}$ and $Y = WR^2$.

Symbols represent the rescaled experimental data for n-C$_8$ and n-C$_{10}$.

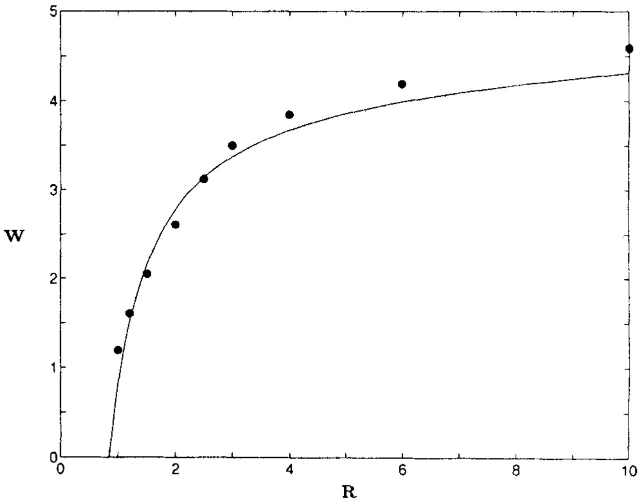

Figure 15. Experimental data (●) for the wt. % W of precipitated asphalt vs. predictions of scaling equation (Eq. 23), with n-C$_5$ as the solvent; R is the solvent-to-crude-oil ratio.

Onset of Precipitation

From a practical point of view, an important quantity is R_c, the value of R at the onset of precipitation. For $R < R_c$ no precipitation occurs, whereas for $R \geq R_c$ one has asphalt or asphaltene precipitation, which causes severe problems for enhanced oil recovery and catalytic coal liquefaction. In general, R_c depends on the pressure and temperature of the system, as well as the compositions of the crude oil and the solvent, or that of the natural gas used for enhanced oil re-

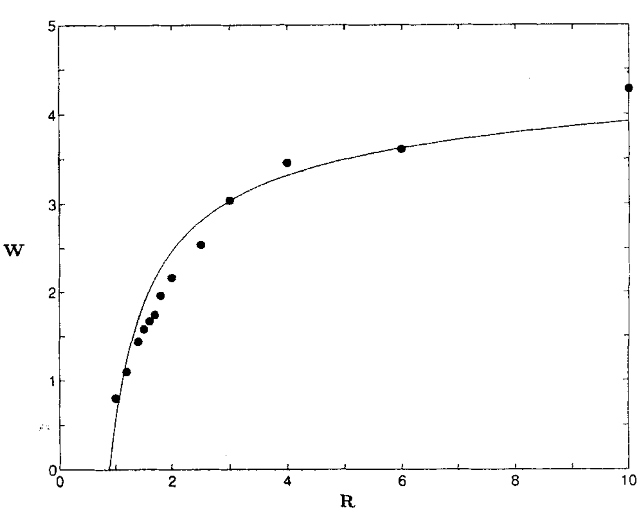

Figure 16. Same as in Figure 16, but with n-C$_6$ as the solvent.

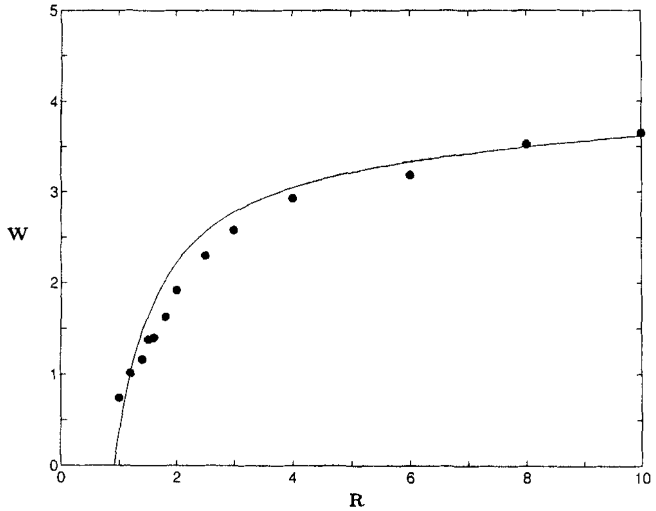

Figure 17. Same as in Figure 16, but with n-C_7 as the solvent.

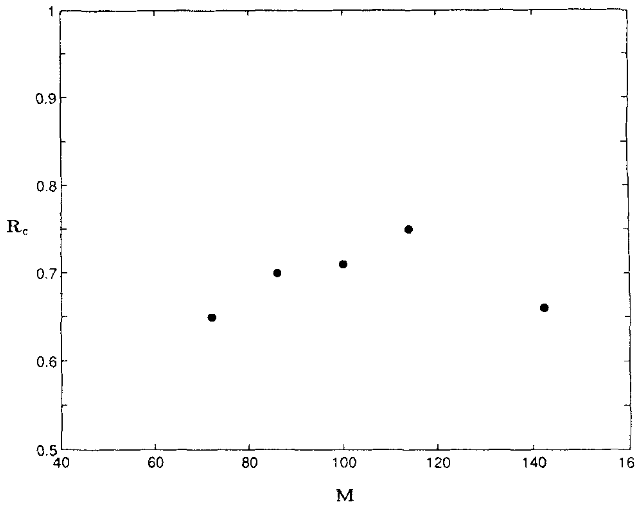

Figure 19. Onset of precipitation R_c as a function of the molecular weight of the solvent.

The data are obtained by extrapolating the results of Figure 1 to $W = 0$.

covery. Currently, the only experimental data for R_c that we are aware of are those of Hotier and Robin (1983), which according to them are subject to great uncertainty. Hirschberg et al. (1984) quote very limited data for R_c, but they do not specify the temperature of their system. From extrapolation of our data shown in Figure 1 to $W = 0$, we can estimate the critical R_c for the onset of precipitation for various solvents. The results are shown in Figure 19. The trend of these results is consistent with that of Hotier and Robin (1983). Moreover, using our scaling equations, we also can predict the onset of the precipitation. To do this, we set $Y = 0$ in the scaling equations and calculate the critical value X_c for the onset of precipitation. Since we have collapsed the data onto a single curve, the value of X_c *must be the same* for all solvents. Indeed, Eq. 21 predicts that $X_c \simeq 0.265$, Eq. 22 yields $X_c \simeq 0.273$, and Eq. 23 gives $X_c \simeq 0.287$, where the difference between the three values is entirely due to the uncertainty in the data. Taking a simple average of the three values, we propose that at the onset of precipitation, $X_c = R_c/M^{1/4} \simeq 0.275$, or

$$R_c = 0.275 M^{1/4}. \tag{24}$$

Equation 24 tells us that *at the onset of precipitation, the critical ratio R_c depends only on the molecular weight of the injected solvent or gas*, at least for the solvents (normal alkanes) that we used in our experiments. More generally, we write Eq. 24 as $R_c = cM^{1/4}$, in which we believe that c is a temperature-dependent quantity. This will be discussed in Part II of this article. Using Eq. 24, we present in Figure 20 the dependence of R_c on M. Note that, unlike Figure 19, Eq. 24 does

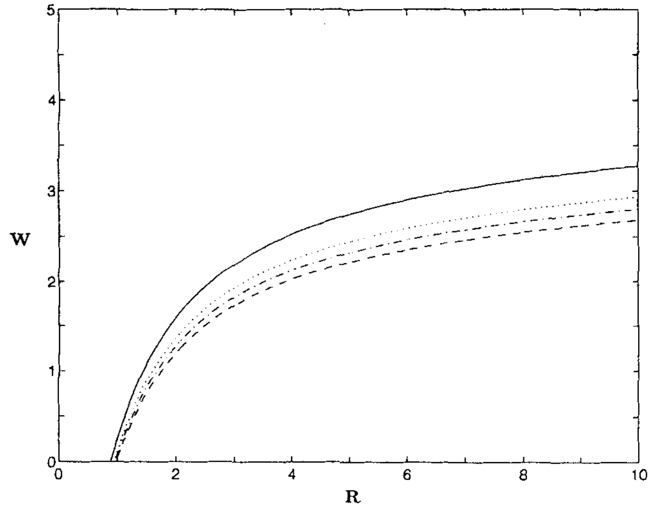

Figure 18. Predictions of scaling equation (Eq. 21) for the wt.% W of precipitated asphalt as a function of the solvent-to-crude-oil ratio R.

The results are from top to bottom for n-C_9, n-C_{11}, n-C_{12}, and n-C_{13}.

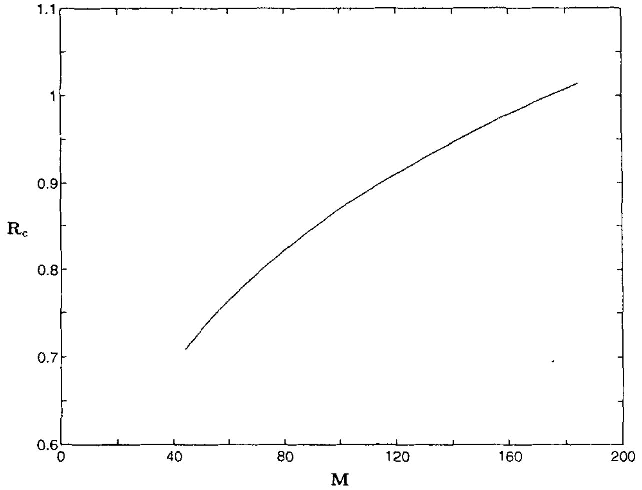

Figure 20. Predicted onset of precipitation R_c as a function of molecular weight M of the solvent.

not indicate the existence of a maximum for R_c, although the difference between the experimental values of R_c for C_8 and C_{10} shown in Figure 20 is small. Moreover, the results of Figure 20 were obtained by extrapolating the data to $W=0$, and the accuracy of this extrapolation is difficult to assess. It would be very important to carry out precise experiments with other types of solvents to further test the accuracy of Eq. 24.

Summary and Conclusions

In this article we presented extensive new experimental data for the onset and amount of asphalt precipitation at atmospheric pressure. A thermodynamic model that uses the Flory–Huggins theory of polymer solutions and an equation of state was also used for predicting the experimental data, and its predictions were found in disagreement with the data. As an alternative, we proposed a simple scaling equation that appears to be capable of providing accurate predictions for the data. Moreover, the scaling equation provides a particularly simple, and apparently universal, prediction for the onset of precipitation.

In Part II of this article we will discuss the behavior of asphalt and asphaltene precipitation at higher values of the ratio R, and elevated temperatures, pressures, and crude-solvent mixture times, close to those of oil reservoirs. Under such conditions, asphalt and asphaltene formation may be similar to aggregation and gelation phenomena. Such phenomena possess fractal and scale-invariant properties, and in fact the existence of scaling equations such as those proposed in this article are precisely due to such fractal properties. In Part II we will study and test our model for such conditions in order to understand its origin and generality, propose mechanisms of asphalt and asphaltene aggregation, carry out computer simulations of formation of such aggregates, and compare the results with the experimental data.

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