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The Influence of Antisolvent Properties on the Initial Settling Rate of Mineral Matter in Solvent-Refined Coal

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Abstract

Addition of antisolvents to coal liquids causes asphaltenes and/or preasphaltenes in the oil to precipitate. The precipitated asphaltenes then agglomerate the particles, causing an increase in the sedimentation rate. A new experimental system has been developed which utilizes time sequenced x-ray photographs of the mineral matter settling in a chamber at high temperature (up to 400°C) and high pressure (400 psig). Experiments were carried out with Solvent Refined Coal filter feed obtained from the Pilot Plant in Wilsonville, Alabama. Initial settling rate data are presented for a variety of antisolvents and are correlated with a linear combination of their carbon to hydrogen ratio and solubility parameter. The advantage of this correlation over the ones proposed earlier is that it involves the use of more fundamental and readily available properties of the antisolvent. The molar weight averages of the carbon to hydrogen ratio and solubility parameter can be used to predict mixture effects for hydrocarbon antisolvents.

INTRODUCTION

Antisolvent precipitation and sedimentation is one of several separation schemes being considered in the commercial development of coal liquefaction processes. These processes have as their goals the production of fuels which are convenient to handle and which meet the specifications

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regarding ash and sulfur boiler and gas turbine fuels. The mineral matter concentration must be reduced to 0.4 wt-% for boiler fuels and to 0.1 wt-% for gas turbine fuels. Depending on the process and the amount of solvent recycle involved, the mineral matter content in coal-derived liquids ranges from 3 to 21 wt-%.

Solvent Refined Coal (SRC) filter feed, obtained from the SRC pilot plant in Wilsonville, Alabama, was used in this study. The SRC contains three parts of recycle solvent for each part of coal. The coal-derived asphaltenes and preasphaltenes are of considerable importance in the behavior of coal-derived liquids. Coal-derived asphaltenes have lower molecular weights than asphaltenes from petroleum origin and have a strong influence on the viscosity of the liquefied coal. Addition of antisolvents causes the precipitation of asphaltenes and preasphaltenes which promote agglomeration.

The mineral matter in coal-derived liquids consists primarily of silicates and iron sulfides. Their physical characteristics are influenced by the oil and hydrocarbon coating on the particles (*1*). Jacques and Henry (*2*) by electrophoretic mobility measurements have shown that these particles carry a net positive charge.

One of several separation schemes is the antisolvent agglomeration and sedimentation (*3*, *4*). There are a number of variables such as temperature, type of antisolvent, antisolvent dose, and mixing conditions. The influence of mixing on antisolvent agglomeration has been studied extensively for Soltrol-130 and is reported elsewhere (*5*). The other variables such as type of antisolvent, antisolvent dose, and temperature will be discussed. An attempt will be made to correlate the effectiveness of various antisolvents (as evidenced by an increase in the initial settling rate) with antisolvent properties such as solubility parameter, hydrogen bonding, dielectric constant, carbon to hydrogen ratio, etc.

PREVIOUS WORK

Previous studies of antisolvent-induced agglomeration and sedimentation of particles in coal-derived liquids (*3*, *4*, *6*–*12*) involved the use of some type of sedimentation device with the direct sampling of the liquid at various times and/or depths, followed by a chemical analysis for ash and sulfur content. The Conoco Coal Development Corp. (*3*, *4*, *6*, *7*) has done considerable experimentation on the use of antisolvents (paraffinic materials) like *n*-decane, Soltrol-130, and process-generated light solvent with antisolvent to oil ratio of 0 to 0.6 by weight. The details of their experiments can be found in Table 1. The experiments were carried out at 260 to 315°C, and direct sampling and chemical analysis were adopted to get settling information. Gorin et al. (*3*, *4*) found that, on a weight basis, *n*-paraffins from *n*-butane to *n*-decane, cyclohexane, and decalin were equally effective in deasphalting and reducing the ash content of a consol synthetic fuel. However, the relative effect of these antisolvents on settling rate has not been discussed.

Rodgers et al. (*8*, *9*) at Oak Ridge National Laboratory performed a considerable number of preliminary experiments with antisolvents like toluene, *n*-decane, wash solvent, and light oil. The experiments were carried out at 150 to 250°C, which is below the desired process operating temperature (260 to 315°C). The results of those experiments suggested that toluene was an effective antisolvent at a dose of 20% by weight of SRC.

Argonne National Laboratory (*10*) also investigated the influence of antisolvents on the separation of solids from synthoil. Experiments were carried out at 150 to 250°C with antisolvents like *n*-hexane, *n*-octane, #2 fuel oil, kerosene, toluene, tetralin, and tetrahydrofuran. The antisolvent dose was 20 to 30% by weight of synthoil. They have found that kerosene is an effective antisolvent for the synthoil gross product.

The Lummus Co. (*11*) has developed a process for the removal of ash from coal liquids by the addition of antisolvents like kerosene distillates. Their pilot plant studies involved heating the coal liquids and antisolvents to operating temperature in the 150 to 315°C range. The two streams were fed continuously. After about 20 hr of continuous operation, the overflow and underflow were collected and then analyzed for solids. The solids content of the overflow was found to satisfy most ash removal criteria with little or no further processing. The ash removal efficiency of the antisolvents is correlated with their paraffinicity/aromaticity as measured by the Watson characterization factor. The typical range of these factors in their study is from 9 to 12, and the higher the value, the better it behaves.

Kerr-McGee Corp. has also been involved in the development of a process for the separation of ash from coal-derived liquids (*12*). Their patents indicate that this process is again a solvent precipitation technique using a supercritical solvent. The details of their studies are not available, but the drop in density of the liquid phase appears to be important.

The previous work can be summarized to indicate that antisolvent-induced agglomeration and sedimentation is a potential separation scheme for removal of mineral matter from coal-derived liquids. It can

TABLE 1

Comparison of Previous Work on Antisolvent Agglomeration and Sedimentation

	Gorin et al. (*3, 4*), CONOCO	Rodgers et al. (*3, 9*), Oak Ridge	Huang and Fisher (*10*), Argonne	Snell and Simone (*11*), Lummus	Burke (*6*), CCDC
Temperature range, °C	260–315	150–250	150–250	150–315	285–315
Antisolvents	*n*-Decane 16% H_2SO_4	Toluene *n*-Decane Wash solvent Light oil	*n*-Hexane *n*-Octane #2 fuel oil Kerosene Toluene Tetralin Tetrahydrofuran	Kerosene Distillates	Soltrol-130 Light solvent (process generated)
Antisolvent Dose, wt-%	0–36	0–20	20–30	40–100	40–60
Settler	Autoclave	2.4 cm i.d., 44 cm tall tube	1.9 cm o.d., 40 cm tall copper tube	Thickener	12 cm i.d., 20 cm in height
Technique	Traveling probe sampling	10 fractions chemical analysis	6 fractions chemical analysis	Chemical analysis of overflow and underflow	4 fractions chemical analysis
Initial settling rate	15–290 cm/hr	~18 cm/hr	—	—	30–150 cm/hr
Correlation for ash removal efficiency of antisolvents	—	—	—	3 antisolvents correlated with Watson characterization factor	Initial settling rate correlated with kauri-butanol number (*7*)
Type of oil used	Hydroextraction effluents	SRC filter feed	Synthoil	Liquefied by hydrogenation	SRC filter feed
Type of coal	Illinois #6 Pittsburgh #8	Illinois #6 Pittsburgh #8	—	Illinois #6	Monterey coal
Mixing speed	600–890 rpm	—	Hand-shaking	—	400 rpm
Mixing time, min.	40	45	10	—	30

also be concluded that the variety of antisolvents which could be potential precipitants has not been investigated because thus far the experimental techniques have been too time consuming and expensive to permit extensive screening of various antisolvents. Except for the Lummus correlation of the Watson characterization factor of antisolvents with their ash-removal efficiency and Conoco's correlation of initial settling rate with the kauri-butanol number of various antisolvents, no other correlation is available.

A new experimental technique developed in our laboratory (*13*, *14*) utilizes time sequenced x-ray photographs of mineral matter settling in a chamber at high temperature and pressure. By using this apparatus it is possible to study rapidly such variables as antisolvent type, antisolvent dose, temperature, and mixing. Finally, the effectiveness of various antisolvents (as evidenced by an increase in the sedimentation rate) will be correlated with such fundamental properties of the antisolvents as solubility parameter and carbon to hydrogen ratio.

THEORY OF SOLUTIONS

Solubility Parameter

In 1916, Hilderbrand developed the concepts of solubility. He advanced the idea that a molecule will be attracted most effectively by other molecules that have the same internal pressure. Solubility parameter is the square root of the internal pressure. If a solute molecule is surrounded by solvent molecules that have the same internal pressure, it will be an ideal solution. On the other hand, if the internal pressures are sufficiently different, then the molecules with the greater internal pressure will cling to themselves and exclude from among themselves the molecules with the lower internal pressure, and immiscibility will result.

Hydrogen Bonding

Solvents are classified into three categories: weakly hydrogen bonded, moderately hydrogen bonded, and strongly hydrogen bonded. In certain cases a similarity of solubility parameter did not assure an equal balance of hydrogen bonding forces.

Dipole Moment

Dipole moment is the product of an electrical charge and a distance, and every polar molecule must contain a positive and negative charge separated by a distance. Dipole moments are measures of the electrostatic imbalance of a molecule. Symmetrical molecules such as methane and benzene are in balance and thus have a zero dipole moment. Unsymmetrical molecules such as ethanol are out of balance electrostatically. Ethanol has a dipole moment of 1.7 Debye units.

Dielectric Constant

Dielectric constant can probably be regarded as the most direct evidence of polarity. The nitro group is highly polar as shown by nitrobenzene with a dielectric constant of 34.8, but in tetranitromethane, whose dielectric constant is 2.1, these polar groups balance each other, leaving little electric moment as a whole. The distinction between the polarity of the molecule and the polarity of the bond serves as a caution against relying solely upon the dielectric constant as an indication of polarity in connection with the problem of solubility.

Carbon–Hydrogen Ratio

In the case of hydrocarbons the atomic carbon to hydrogen ratio can be used to correlate the effectiveness of solvents. The carbon to hydrogen ratio is a measure of the paraffinicity/aromaticity of hydrocarbon liquids. However, caution must be made against compounds like benzene and styrene which have C/H ratios equal to one but are structurally different. Hence the C/H ratio alone will not explain the behavior of various antisolvents, but it might in conjunction with other parameters like solubility parameters, hydrogen bonding, dipole moment, or dielectric constant.

Watson Characterization Factor

Watson and Nelson (*15*) suggested a characterization factor, W, as a measure of the paraffinicity/aromaticity of hydrocarbon liquids and petroleum fractions. The characterization factor was defined as

$$W = \sqrt[3]{T_b}/G \tag{1}$$

where T_b is the molar average boiling point of the liquid in °R, and G is the specific gravity of the liquid (60°F/60°F). More paraffinic materials have values higher than 12 for the characterization factor, as reported in Table 4 (see below).

Kauri-Butanol Value

Kauri-butanol number is a measure of the relative solvent power of hydrocarbon solvents having a boiling point over 40°C. According to ASTM standard D1133 (*18*),

$$\text{Kauri-butanol value} = 65\frac{C - B}{A - B} + 40 \tag{2}$$

where A = milliliters of toluene required to titrate 20 g of kauri-butanol reagent
B = milliliters of heptane–toluene blend required to titrate 20 g of kauri-butanol reagent
C = milliliters of sample required to titrate 20 g of kauri-butanol reagent

For kauri-butanol values of 60 and over, the standard is toluene and has an assigned value of 105. For values under 60, the standard is a blend of 75% *n*-heptane and 25% toluene and has an assigned value of 40.

EXPERIMENTAL

Equipment

The equipment used in this study is shown in Fig. 1, and the details can be found elsewhere (*13*, *14*). Briefly, the coal liquid can be heated to the desired temperature in a 300-ml Parr Instrument Autoclave. The autoclave can be heated to a maximum temperature of 673°K and can withstand up to 1.4×10^7 Pa (2000 psig). An electric motor produces a continuous range of impeller speeds from 0 to 1000 rpm.

The sedimentation cell is designed to handle pressure up to 2.75×10^6 Pa (400 psig) and temperatures up to 673°K. The temperature is measured at four points on the cell and is controlled manually with a powerstat. Thin aluminum windows (0.15 cm) are used for x-rays to penetrate. All valves between the autoclave and the sedimentation chamber have large ports to prevent the breakup of agglomerates upon transfer.

A Diano Corp. x-ray system is employed. Eight exposures can be made per film per experiment. An E-C Corp. densitometer connected with a Seargent-Welch recorder interprets the x-ray film.

Two high-pressure, high-temperature Millipore filter holders are used to filter the treated coal-derived liquid. The first filter holder contains

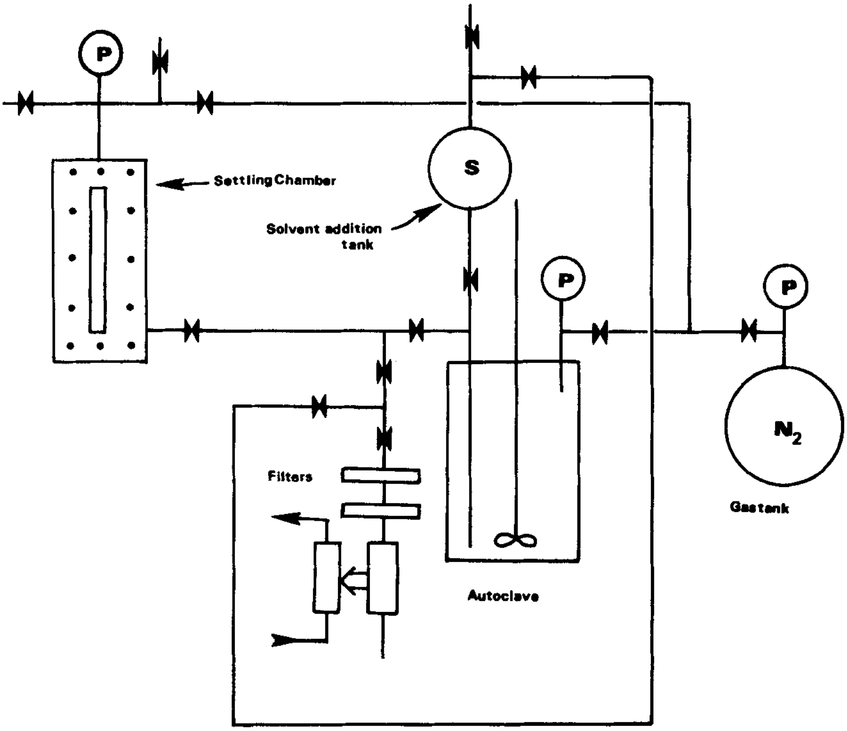

FIG. 1. High-pressure, temperature sedimentation apparatus.

a 5-μm Mitex (Teflon) filter and the second a 0.7-μm glass fiber filter. Previous work has shown that once a small cake was formed, the majority of small and large particles were trapped. The second filter trapped any small particles passing the first filter paper. The filters and tubing were heated with heating tape. A heat exchanger was employed downstream of the filters to cool the treated oil before it was collected in an open container.

Materials

SRC filter feed was obtained from the Wilsonville SRC Pilot Plant in Wilsonville, Alabama. Tables 2 and 3 indicate the properties of SRC filter feed and SRC light distillate, which is a process-generated solvent. Table 4 lists important properties of various antisolvents used in this study.

TABLE 2

Properties of SRC

Laboratory sample number	2001
Feed coal	Monterey coal
Approximate boiling range	205–480°C
Average molecular weight	230
Viscosity (solids free)	3.4 cP at 395°K 1.9 cP at 450°K
Cresol insolubles	3.49%
Ash	2.37%
SRC	13.5% SRC in filter feed
Elemental analysis: % by wt	
Carbon	87.2
Hydrogen	7.9
Sulfur	0.3
Nitrogen	0.9
Oxygen	3.9

TABLE 3

Properties of SRC Light Distillate

Laboratory sample number	13732
Feed coal	Kentucky #9 and #14
Approximate boiling range	37–205°C
Elemental analysis: % by wt	
Carbon	84.0
Hydrogen	11.5
Sulfur	0.2
Nitrogen	0.4
Oxygen	3.9

Procedure

Sedimentation

The sedimentation chamber shown in Fig. 1 is pressurized with nitrogen and then heated to the operating temperature. During this process the autoclave is charged with coal liquid (about 100 ml) and brought to the operating temperature. Unheated antisolvent is added to the charged autoclave, the contents of which are then mixed at specific conditions. It is then transferred to the sedimentation cell by using a pressure difference between the cell and the autoclave. The amount of liquid in the cell is calculated from the gas effluent measured with a wet test meter which is

TABLE 4

Properties of Various Antisolvents

Antisolvent	Solubility parameter	Hydrogen bonding	Dipole moment	Dielectric constant	C/H ratio	Watson characterization factor	Kauri-butanol value
n-Pentane	7.0	0.0	0.0	1.84	0.416	13.06	26
n-Hexane	7.3	0.0	0.0	1.89	0.428	12.90	30
n-Heptane	7.4	0.0	0.0	1.93	0.437	12.79	37
n-Decane	6.6	0.0	0.0	2.00	0.454	12.74	25
Hexadecane	8.0	—	—	2.52	0.470	12.97	49
Dipentene	8.5	1.5	0.0	2.30	0.625	11.10	64
Cyclohexane	8.2	0.0	0.0	2.02	0.500	11.04	54
Methyl-cyclohexane	7.8	0.0	0.3	3.22	0.500	11.39	46
Benzene	9.2	0.0	0.0	2.28	1.000	9.78	110
Styrene	9.3	1.5	0.0	2.43	1.000	9.98	95
Toluene	8.9	4.5	0.4	2.38	0.875	10.20	105
Cresol	11.3	—	—	11.50	1.000	9.20	—
Nitrobenzene	10.0	2.8	4.3	34.80	1.200	7.93	—
Light solvent	—	—	—	4.60	—	—	—
Recycle oil	—	—	—	—	—	—	—

connected to the valve on top of the settling chamber. The sedimentation process is then monitored by x-ray photography. Pictures were usually taken at intervals of 2, 4, 6, 8, 10, 20, 40, and 60 min. The interface heights are then located as a function of time and plotted. The slope of the constant-rate period of interface height versus time gives the initial settling rate and is reported in cm/hr. The interpretation scheme from x-ray negative to dimensionless plot is shown in Fig. 2.

Filtration

The valves between the autoclave and the filters, as shown in Fig. 1, are opened and the N_2 pressure source is utilized to force the heated coal liquid treated with antisolvent through the filters and the heat exchanger to the atmosphere. The valves are shut off when a certain amount of liquid has passed through the filters. The valve from the nitrogen line is opened and the remaining liquid in the line and filters is forced through the system. The volume and mass of the collected liquid are determined. The filter cakes are removed and dried in an oven at 70°C for several hours and weighed to constant weight. The mass fraction of material which is solid can then be easily calculated.

Specific experimental conditions and procedures are presented with the results and discussion of these experiments.

Reproducibility

n-Decane was selected as the antisolvent for reproducibility studies. Three identical runs were made during the 3-month period of experimentation. The experimental condition chosen was 260°C with 2 min mixing at 550 rpm followed by an 8-min mixing at 250 rpm for the antisolvent/oil ratio of 0.25 by volume. The initial settling rate obtained under these conditions is 36 cm/hr for the first run, 32 cm/hr for the second, and 33.8 cm/hr for the third run. These are within the error associated with the calculations of initial settling rate from interface height versus time plot. The initial curves are very close in the first 20 min and are very difficult to separate as shown in Fig. 3. Separation can occur when the slopes are drawn to the x-axis. In spite of the graphical difficulties, the reproducibility of the *n*-decane experiments is good.

Figure 3 indicates a nonlinear rate of rise of the compacted zone. This might be due to particle segregation when the particles of wide size distribution are involved (*16*). Under these conditions the assumption of a unique relationship between settling rate and solids concentration

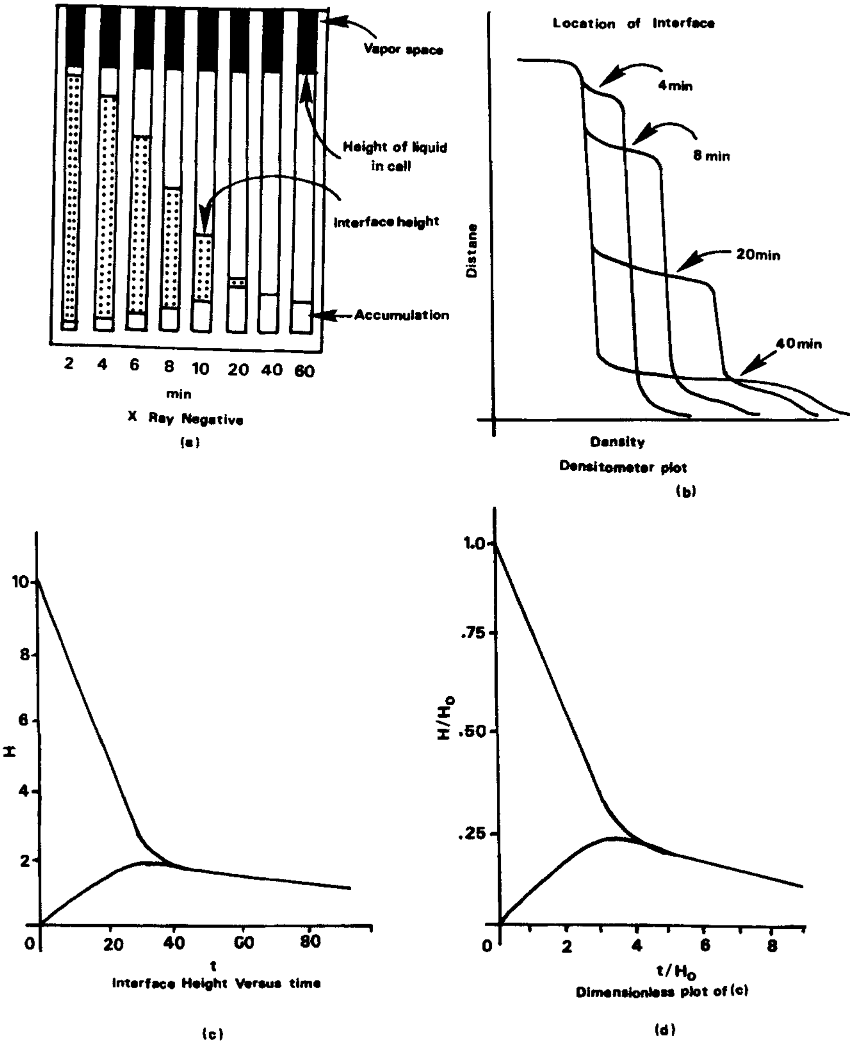

FIG. 2. Interpretation of data from x-ray negative.

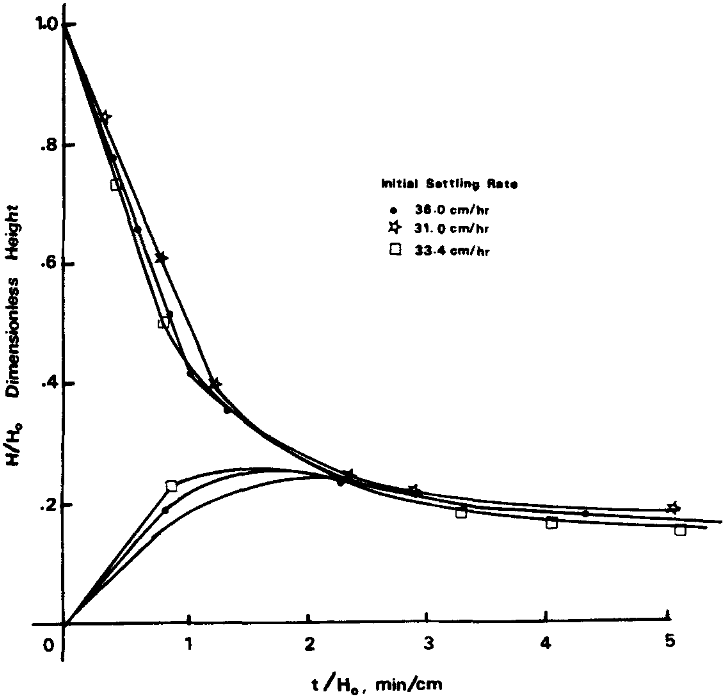

FIG. 3. Reproducibility of initial settling rate for SRC–*n*-decane system at 260 °C with a 2-min mixing at 550 rpm followed by an 8-min mixing at 250 rpm for antisolvent/oil ratio of 0.25 by volume.

is unlikely to apply in the compression region. The settling rate will also be a function of particle size and size distribution. Efforts are presently underway to explain this phenomenon.

RESULTS AND DISCUSSION

Influence of Antisolvent

Preliminary investigation with four different antisolvents was carried out to understand the influence of antisolvents, under identical conditions, on the initial settling rate and the compact zone. The antisolvents selected were *n*-decane, light solvent, recycle oil, and cresol. The base condition was chosen as 260 °C, with a 2-min mixing at 550 rpm followed by an

8-min mixing at 250 rpm for the antisolvent/oil ratio of 0.25 by volume. Sequential mixing was found to be more advantageous than a single impeller speed (*5*). Because of the high volatility of light solvent, some difficulty was experienced in getting the solvent into the autoclave, and hence the antisolvent/oil ratio is less than 0.25 by volume. Recycle oil gives a sedimentation rate which is significantly lower than *n*-decane as would be expected because recycle oil is the main component of the SRC filter feed, and thus should cause little precipitation. On the other hand, cresol greatly increases the sedimentation rate. It was suspected that cresol dissolved off naturally occurring asphaltic materials and consequently increased the sedimentation rate (*17*). A comparison of these four antisolvents is shown in Fig. 4.

Figure 5 depicts the compacted solids height as a function of time for

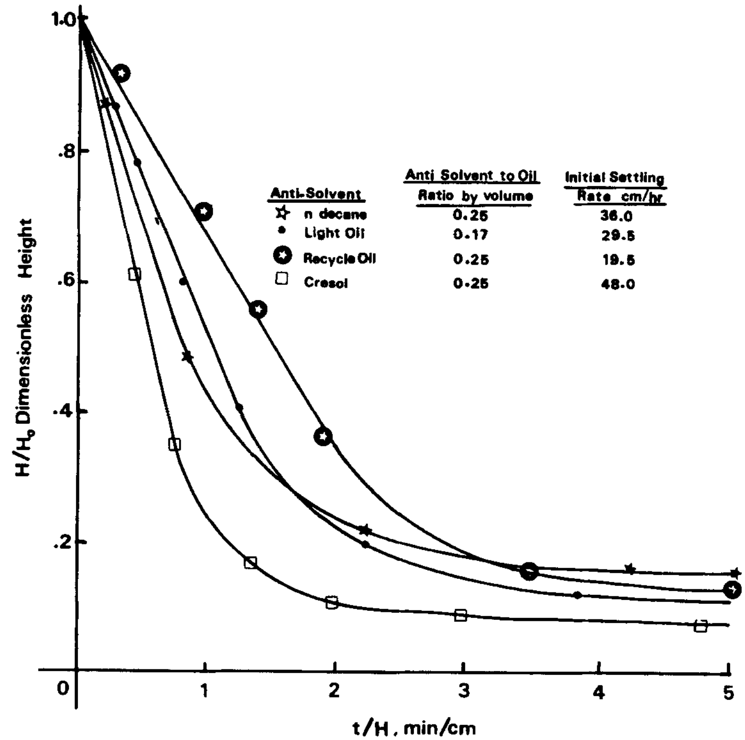

FIG. 4. Influence of different antisolvents on initial settling rate at 260°C with a 2-min mixing at 550 rpm followed by an 8-min mixing at 250 rpm.

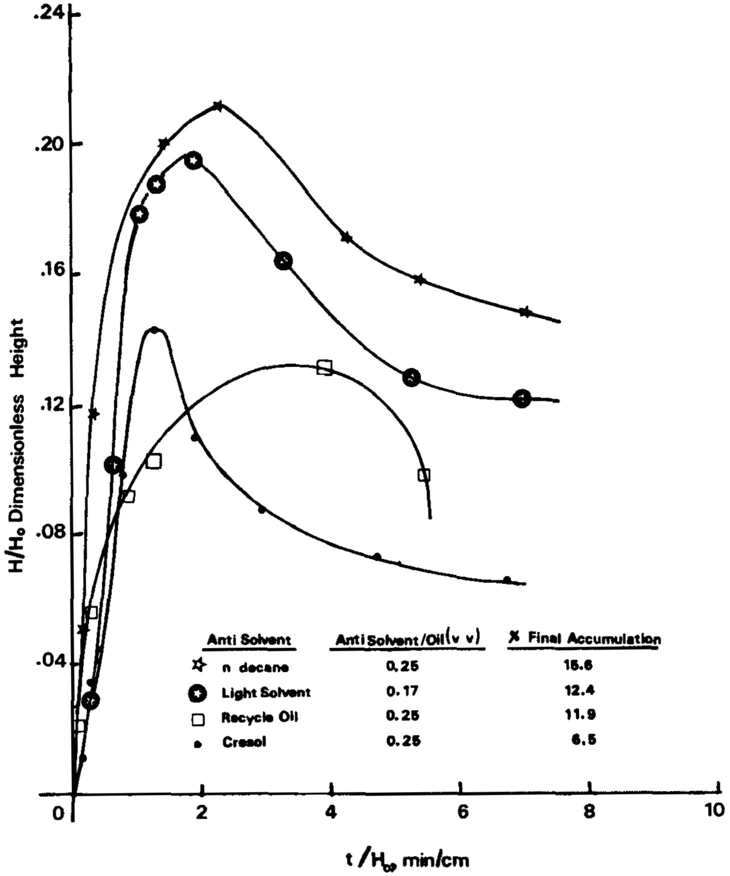

FIG. 5. Influence of different antisolvents on accumulation of solids at 260 °C with a 2-min mixing at 550 rpm followed by an 8-min mixing at 250 rpm.

these four antisolvents. The lower solids volume shown in this figure for cresol seems to indicate that the solids are mainly inorganic matter whereas the solids resulting from the other three solvents contain significant amounts of precipitated asphaltic materials.

Selection of Antisolvents

Antisolvents were selected based on their solubility parameters (6.6–11.3), hydrogen bonding (0–4.5), dipole moment (0–4.3), dielectric constant

(2–35), and Watson characterization factor (9–13). The properties of these antisolvents are presented in Table 4. Filtration studies were carried out both at room temperature and at 205 °C to measure the amount of precipitate resulting from antisolvent addition to SRC filter feed. Room temperature measurements were made by introducing the antisolvent into the coal-derived liquid, stirring, and filtering the slurry on a 0.45-μm Millipore filter. The solid residue which is collected is then oven-dried at 70 °C and atmospheric pressure, and weighed for constant weight. A blank filtration experiment was carried out with SRC filter feed without antisolvent. From the results of these filtration experiments, the weight percent of precipitate was calculated by

$$W_p = \left\{\frac{W_A - W_0}{W_{\text{oil}} - W_0}\right\} \times 100 \tag{3}$$

where W_p = the weight percent of precipitated material with antisolvent addition
W_A = weight of solids with antisolvent addition, g
W_0 = weight of solids without antisolvent, g
W_{oil} = weight of oil filtered (antisolvent free basis), g

The filtration and sedimentation experiments were carried out with these antisolvents at 205 °C with 2-min mixing at 550 rpm followed by an 8-min mixing at 250 rpm for the antisolvent to oil ratio of 0.25 by volume. An operating temperature of 205 °C was selected due to high vapor pressure of some antisolvents like *n*-petane and *n*-hexane. Filtration was carried out by withdrawing a sample from the stirred autoclave and transferring it to a series of two filters as shown in Fig. 1. The first filter has a 5-μm Teflon filter medium. The downstream filter has a 0.7-μm glass fiber filter. The residues from both of these filters are oven-dried at 70 °C and atmospheric pressure, and then weighed to constant weight. A blank experiment with SRC filter feed was also carried out to compute the weight percent of precipitated material with antisolvents according to Eq. (3). The results of these filtration experiments are shown in Fig. 6 which illustrates the influence of the carbon to hydrogen ratio of the antisolvent on the extent of precipitation. Figure 6 indicates that the carbon to hydrogen ratio is a better correlating parameter at room temperature than at 205 °C. This suggests that different oil components are precipitating at the elevated temperature, and parameters, in addition to the carbon to hydrogen ratio, must be considered to improve the correlation of high temperature data.

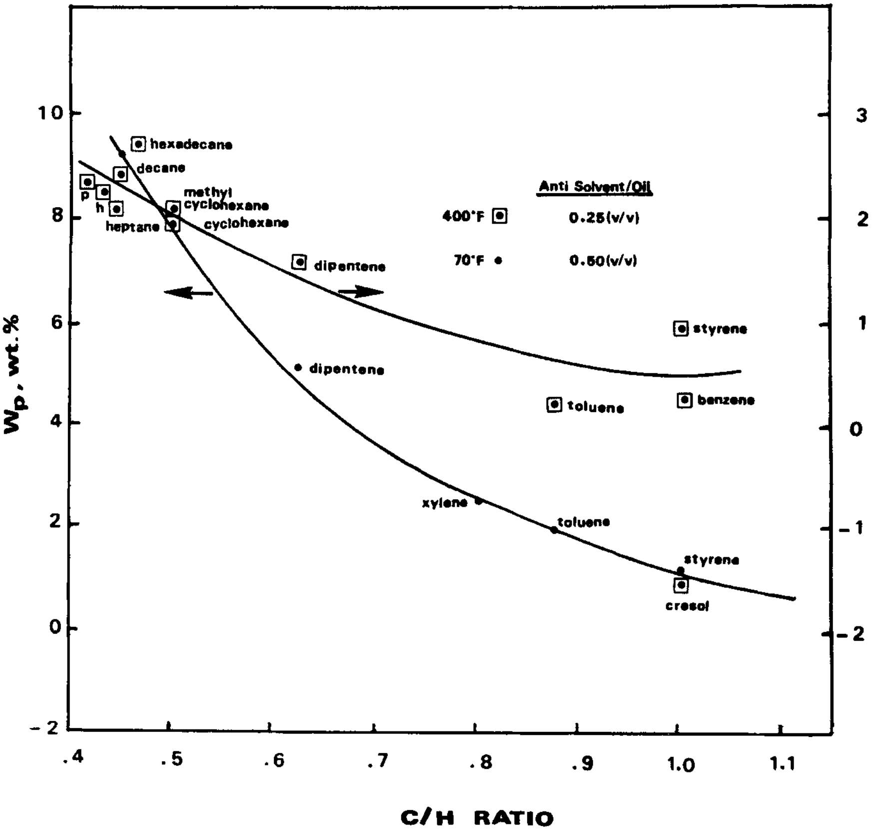

FIG. 6. Influence of carbon to hydrogen ratio of the antisolvents on weight percent of precipitate.

The weight percent of the precipitate resulting from antisolvent addition correlated well with the initial settling rate as shown in Fig. 7, which illustrates that increased precipitation causes increased sedimentation rate through agglomeration. Figures 6 and 7 suggest a correlation between the carbon to hydrogen ratio and the initial settling rate. This is attempted in Fig. 8. Due to scatter in the data, correlation between the initial settling rate and other parameters like solubility parameter, hydrogen bonding, dipole moment, dielectric constant, and Watson characterization factor was attempted. Figure 9 is a plot of Watson characterization factor of the antisolvent versus initial settling rate, and in Fig. 10

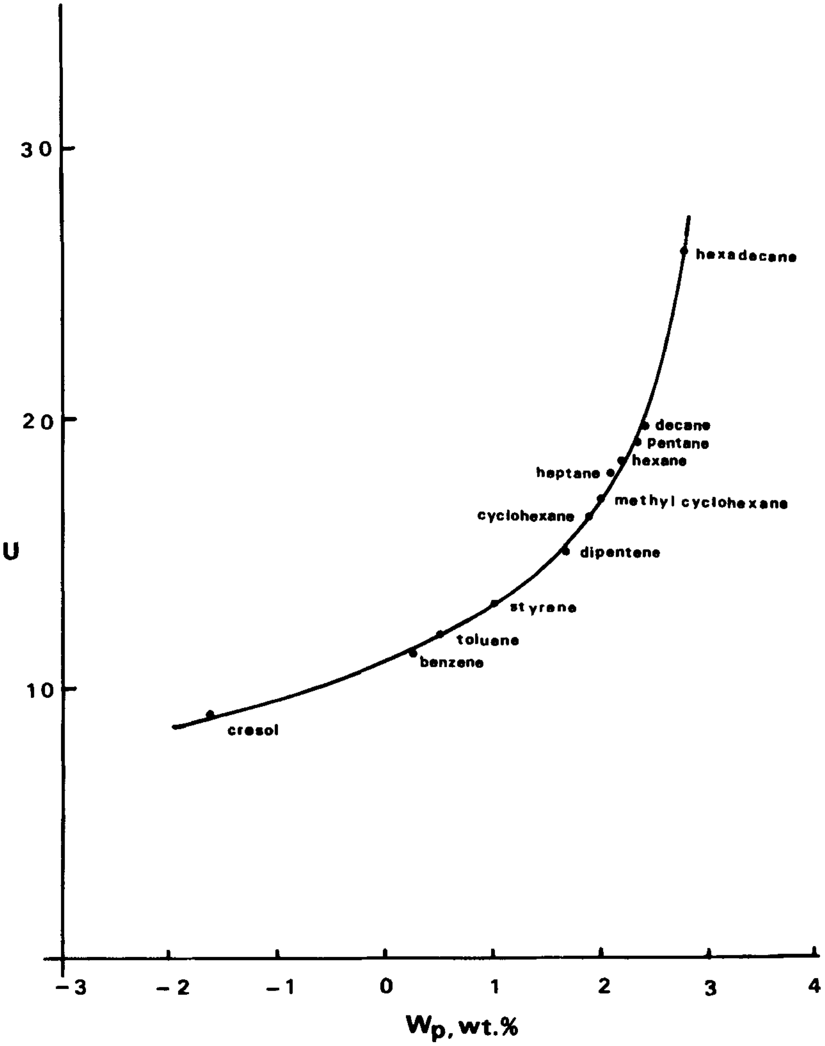

Fig. 7. Influence of the weight percent of precipitated material on the initial settling rate at 205°C with a 2-min mixing at 550 rpm followed by an 8-min mixing at 250 rpm for antisolvent to oil ratio of 0.25 by volume.

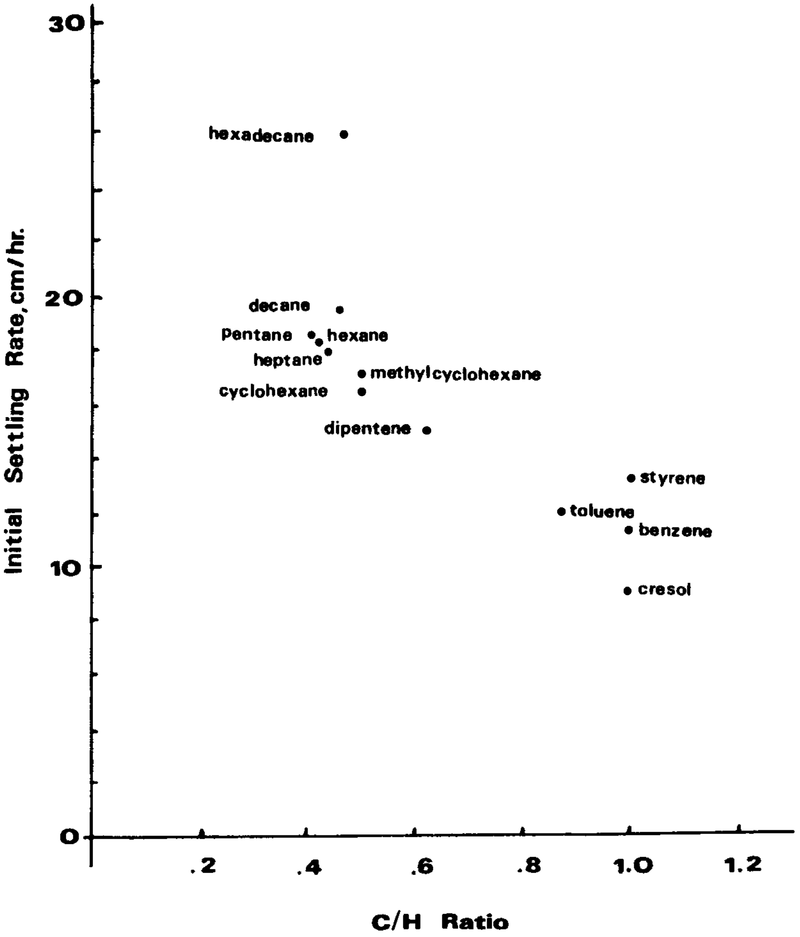

FIG. 8. Influence of carbon to hydrogen ratio of the antisolvent on the initial settling rate (conditions the same as in Fig. 7).

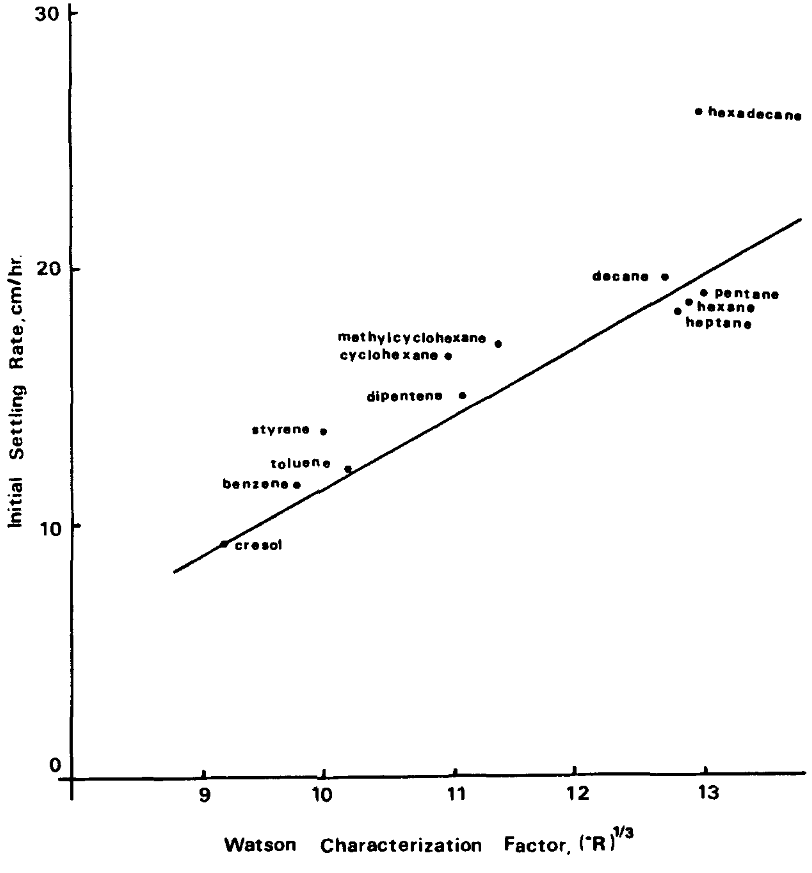

FIG. 9. Correlation of initial setting rate with Watson characterization factor of antisolvent (conditions the same as in Fig. 7).

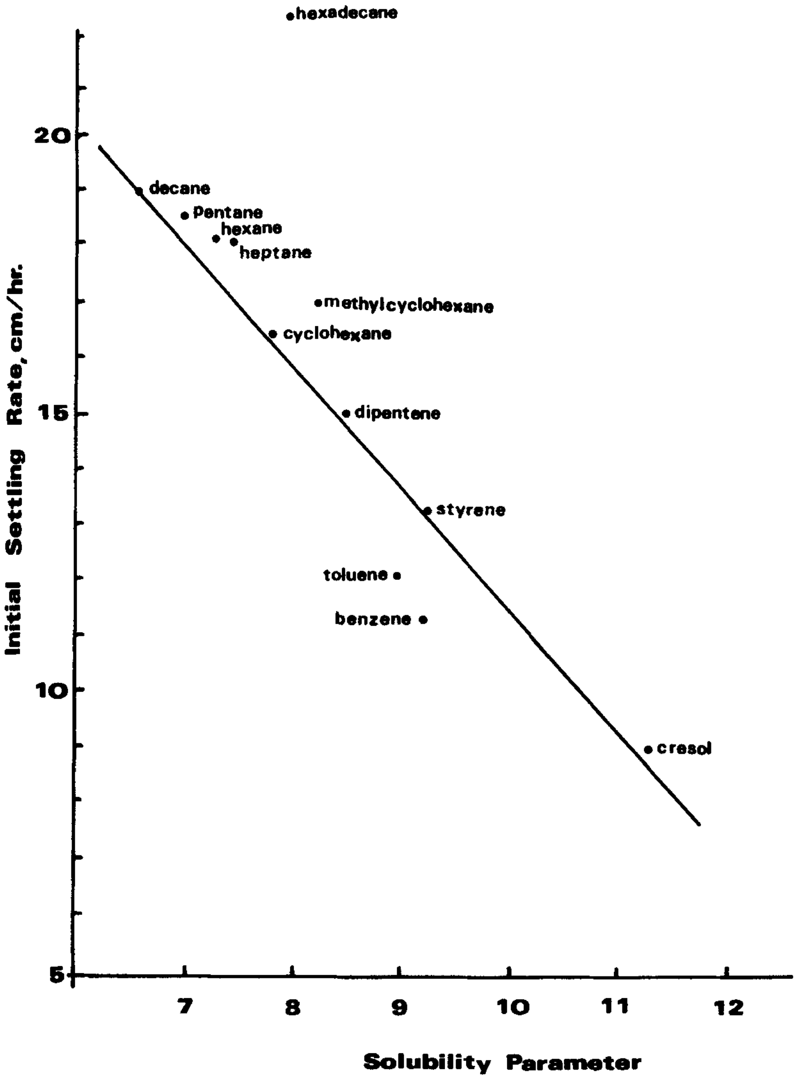

FIG. 10. Correlation of initial settling rate with solubility parameter of the antisolvent (conditions the same as in Fig. 7).

the initial settling rate is plotted against the dispersion component of the solubility parameter of the antisolvent which indicates that the dispersion component of the solubility parameter is a better correlating parameter than the Watson characterization factor. Figures 6, 7, 8, and 10 suggest an empirical correlation of the form

$$U = p(\mathrm{C/H}) + q(\delta) + r \tag{4}$$

The values of the constants through linear regression are found to be $p = -8$, $q = -1.6$, and $r = 33.5$. Therefore,

$$U = 33.5 - 8(\mathrm{C/H}) - 1.6(\delta) \tag{5}$$

The factor on the right-hand side of Eq. (4) can be called *M*. The value of *M* for various antisolvents is plotted against *U*, the experimental initial settling rate as shown in Fig. 11. Cresol does not follow Eq. (5) since it behaves mechanistically differently from other antisolvents. It dissolves the asphaltic coatings on the mineral particles. Nitrobenzene was very interesting in that no settling front could be detected; this might mean that the slurry was stabilized or that settling occurred with no front. It can be seen that hexadecane does not follow any of the correlations, which is unexpected and presently unexplained.

The constants *p*, *q*, and *r* appearing in Eq. (5) should be functions of temperature, antisolvent dose, and type of coal-derived liquid. It can be tentatively concluded that the initial settling rate can be correlated well with two important parameters of antisolvent: the carbon to hydrogen ratio and the solubility parameter. However, more experiments on coal liquefaction products from different liquefaction processes are necessary to establish a generalized correlation that can be readily applicable to every coal liquefaction product.

Initial settling rates for the mineral matter in SRC filter feed with various antisolvents have been correlated previously with the kauri-butanol number of antisolvents (*7*). Since the initial settling rate correlates with the carbon to hydrogen ratio and the solubility parameter of antisolvents according to Eq. (5), a linear combination of the carbon to hydrogen ratio and the solubility parameter of antisolvents should correlate with their kauri-butanol number. Kauri-butanol numbers of various antisolvents were experimentally determined according to ASTM standard D-1133 (*18*). A correlation of the following form can be proposed:

$$K = 80(\mathrm{C/H}) + 16(\delta) - 117 \tag{6}$$

Figure 12 compares the experimental kauri-butanol value with those

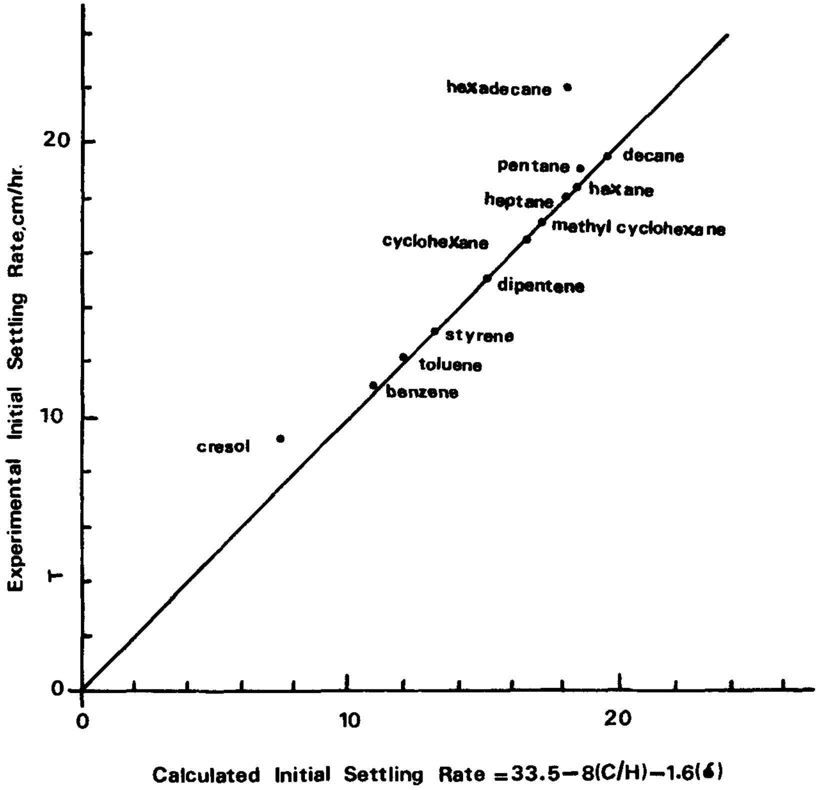

FIG. 11. Correlation of initial settling rate with a linear combination of carbon to hydrogen ratio and solubility parameter of antisolvent (conditions the same as in Fig. 7).

predicted by Eq. (6), and in Fig. 13 the initial settling rate is correlated with the kauri-butanol value. From Figs. 11, 12, and 13 it can be concluded that the carbon to hydrogen ratio and the solubility parameter are the fundamental properties of various antisolvents that influence the antisolvent precipitation and subsequent sedimentation process.

Table 5 compares the percentage standard deviation obtained with the present correlation with those of Lummus (*11*) and Conoco Coal Development Co. (*7*). The advantage of this correlation over the ones proposed earlier (*7*, *11*) is that it involves the use of more fundamental and readily available properties of the antisolvent, i.e., the carbon to hydrogen ratio and the solubility parameter.

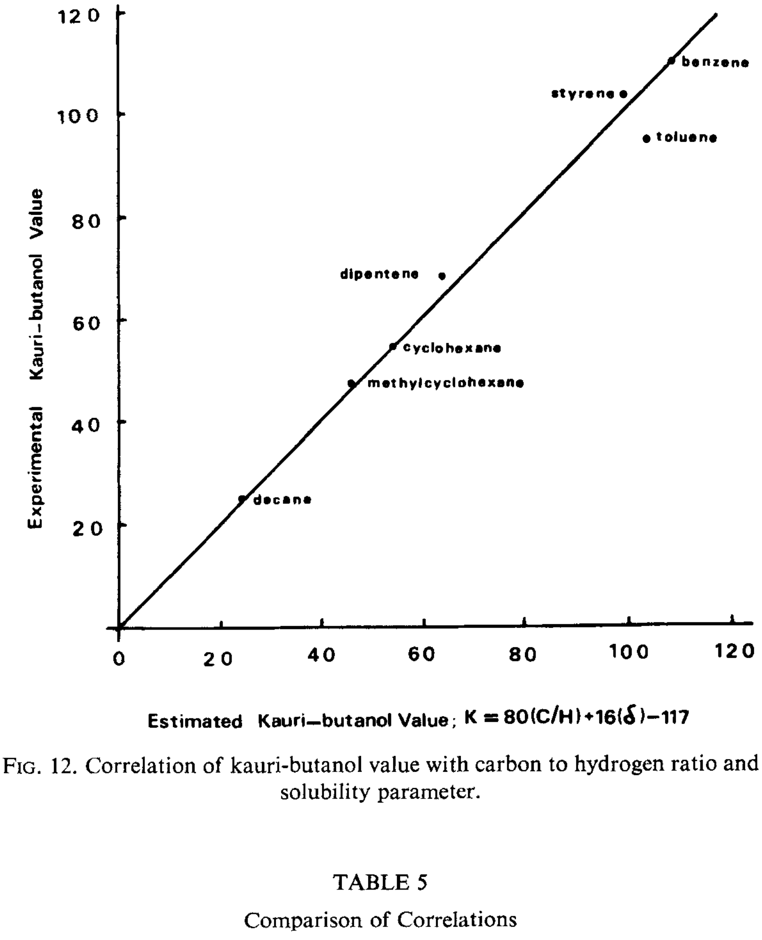

FIG. 12. Correlation of kauri-butanol value with carbon to hydrogen ratio and solubility parameter.

TABLE 5

Comparison of Correlations

Correlation	% standard deviation	% standard deviation (excluding *n*-hexadecane)
$U_0 = 25.7 - 14.9(C/H)$	10.40	8.8
$U_0 = 38 - 2.6(\delta)$	9.20	7.0
$U_0 = 2.8(W) - 15.8$	8.20	7.0
$U_0 = 21 - 0.09(K)$ (excluding *m*-cresol)	4.48	2.1
$U_0 = 33.5 - 8(C/H) - 1.6(\delta)$	5.15	2.5

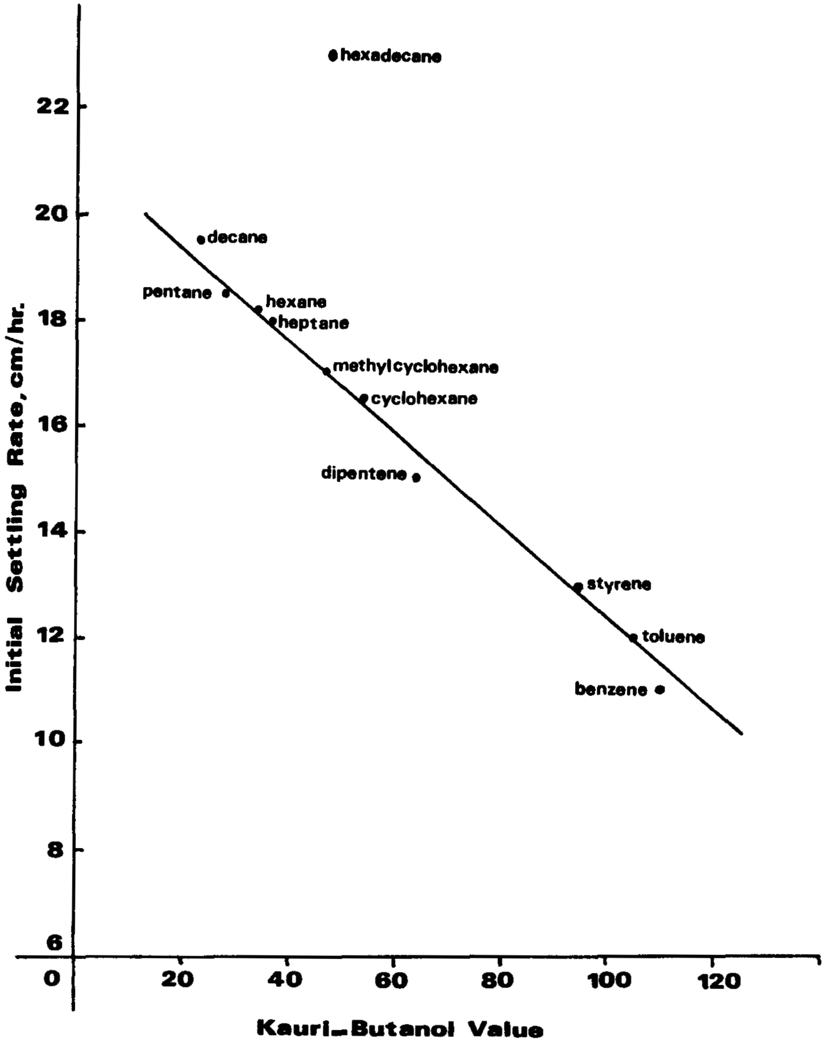

FIG. 13. Influence of kauri-butanol value on the initial settling rate at 205°C with a 2-min mixing at 550 rpm followed by an 8-min mixing at 250 rpm for antisolvent to oil ratio of 0.25 by volume.

Influence of Antisolvent Concentration

Increased antisolvent concentration causes more precipitation of asphaltenes and preasphaltenes in the oil and agglomeration, which would increase the sedimentation rate. The influence of antisolvent concentration was studied for toluene, *n*-decane, and Soltrol-130. The base case for toluene and *n*-decane addition was chosen as 260°C, and sequential mixing at 550 rpm for 2 min followed by an 8-min mixing at 250 rpm. The antisolvent/oil ratios studied were 0.1, 0.25, and 0.5 by volume. In the case of Soltrol-130, the base case was 285°C and 30-min mixing at 550 rpm. Figure 14, which is a plot of initial settling rate versus antisolvent/oil ratio by volume, supports the fact that increased antisolvent concentration causes more precipitation and agglomeration which in turn increases the initial settling rate.

The cross-over in the initial settling versus antisolvent concentration plot for *n*-decane and Soltrol-130 can be explained as follows: Soltrol-130 is a mixture of both light and heavy end hydrocarbons from C_5 to C_{15}. The boiling point is in the range of 185 to 207°C. At the operating temperature of 285°C, as the Soltrol to oil ratio increases, the actual concentration of light ends in the oil phase decreases due to vapor pressure considerations, and only the heavy ends cause precipitation to occur. As more of the light ends leaves the oil phase, the C/H ratio of Soltrol increases, and from Fig. 8 it can be expected that the initial settling rate will be lower than the value when both light and heavy ends are present in the oil phase. In the case of *n*-decane, the C/H ratio of 0.45 is a constant value, and increased *n*-decane concentration increases the initial settling rate.

The initial settling rate obtained with toluene, under identical conditions, is lower than that for *n*-decane. This can be explained by the higher values of the carbon to hydrogen ratio and the solubility parameter for toluene compared with *n*-decane, as can be seen from Table 4.

Mixed Antisolvents

In refinery operations, several cuts of solvents containing a range of hydrocarbons are produced. In most cases it is economically more attractive to use a mixture of antisolvents instead of pure antisolvents like *n*-decane or toluene. The objective of this part of the study was to investigate the influence of mixture antisolvents on the initial settling rate

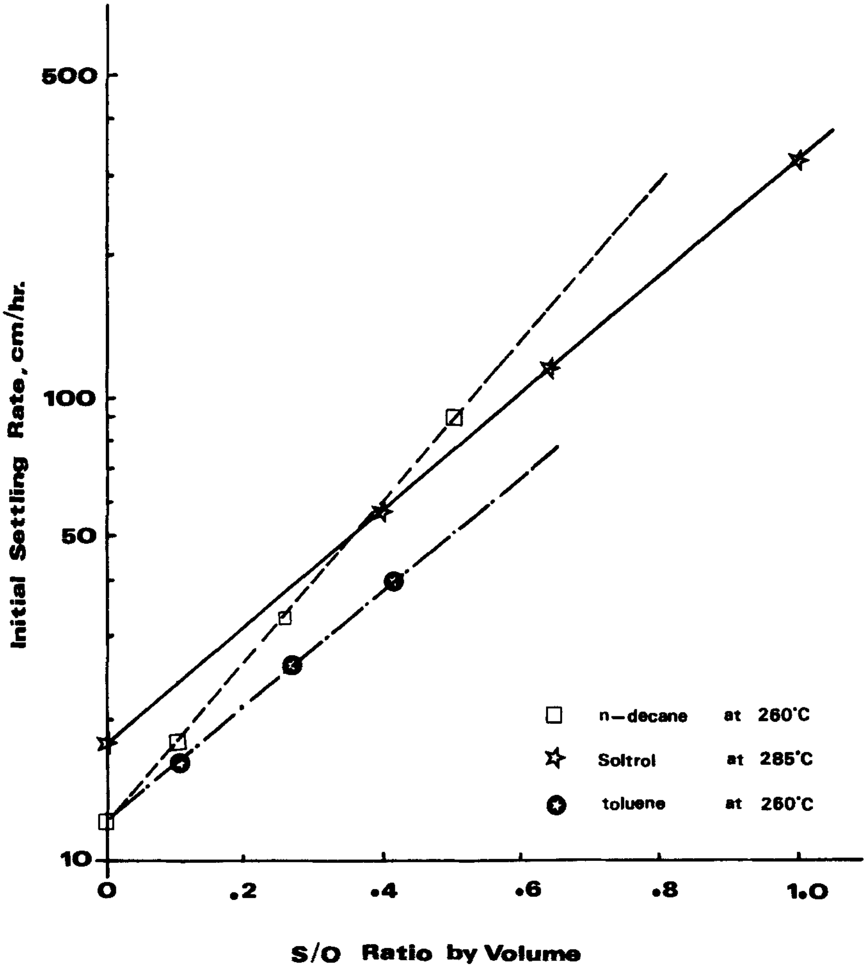

FIG. 14. Influence of antisolvent concentration on the initial settling rate with a 2-min mixing at 550 rpm followed by an 8-min mixing at 250 rpm for *n*-decane and toluene and a 30-min mixing at 550 rpm for Soltrol-130.

and to test the correlation of initial settling rate with a linear combination of carbon to hydrogen ratio and solubility parameter.

Experiments were carried out at 260°C with a 2-min mixing at 550 rpm followed by an 8-min mixing at 250 rpm. A mixture of 50% *n*-decane and 50% toluene by volume was used as antisolvent. One set of experiments was done with the total antisolvent to oil ratio of 0.25 by volume and another with 0.5 by volume. Experiments were also carried out with pure *n*-decane and toluene under these conditions. Independent investigation of the influence of antisolvent dose on the initial settling rate was carried out at 260°C with *n*-decane and toluene. The results indicated a linear relationship between the initial settling rate and the mole fraction of the antisolvent. An average molecular weight of 300 was used for 3:1 SRC in the mole fraction calculations.

The effective carbon to hydrogen ratio and the solubility parameter of the *n*-decane–toluene mixture were calculated by the mole fraction weighting. Figure 15 is a plot of the initial settling rate as a function of a linear combination of the carbon to hydrogen ratio and the solubility parameter of the antisolvent. The influence of mixed antisolvents on the initial settling rate can be predicted with the following information:

(1) The composition of the mixture to calculate the effective carbon to hydrogen ratio and the solubility parameter on mole fraction weighting.
(2) The initial settling rate data for the pure components of the mixture.

The effect of mixed antisolvents is more pronounced at high solvent dose than at low dose.

Influence of Temperature

In this section an attempt has been made to investigate the influence of temperature on the initial settling rate of mineral matter in coal-derived liquids when no antisolvent is present. The four different temperatures considered are 150, 205, 260, and 315°C. From the viscosity values for SRC reported in Table 2, the following equation can be proposed to predict viscosity at other temperatures:

$$\mu = 0.0067e^{2500/T} \qquad (7)$$

where T is in °K.

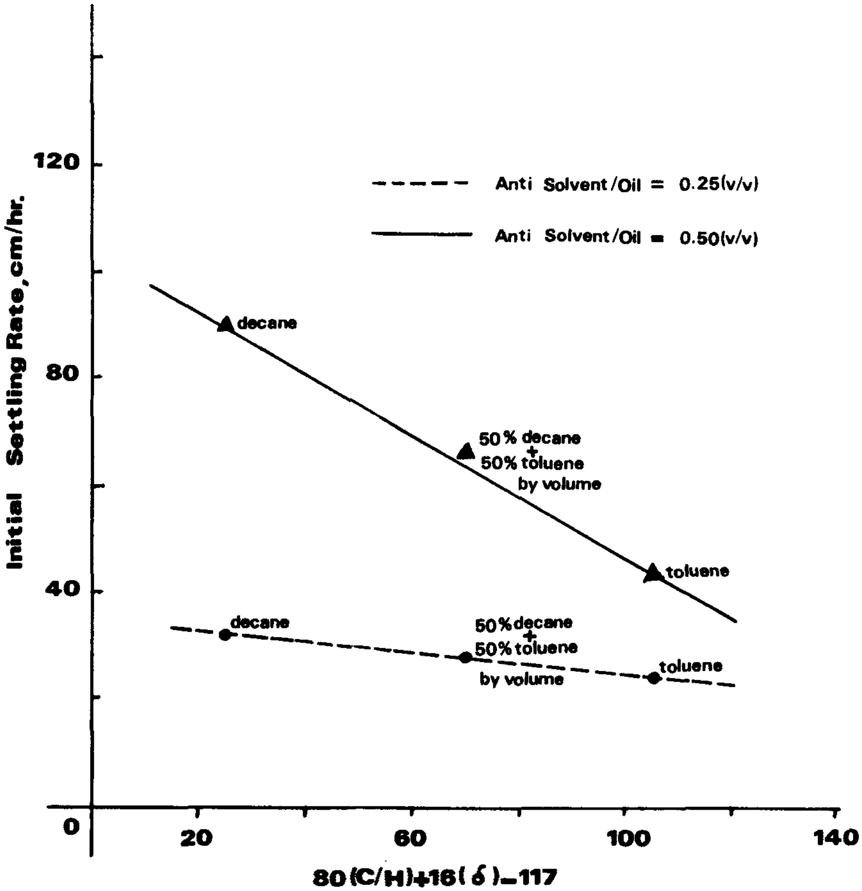

FIG. 15. Influence of a mixture of antisolvents on the initial settling rate at 260 °C with a 2-min mixing at 550 rpm followed by an 8-min mixing at 250 rpm.

Equation (7) is used to obtain viscosity at 150, 205, 260, and 315 °C. Independent calculation shows that Stokes' law is valid. From Stokes' law of hindered settling,

$$U = \frac{\bar{d}_p^2(\rho_s - \rho_l)g}{18\mu} f(\phi) \tag{8}$$

The base condition is selected to be 205 °C since all the experiments with various antisolvents were carried out at this temperature due to vapor pressure limitations. At 205°C

$$\mu_{205^\circ\mathrm{C}} = 0.0067e^{2500/478} = 1.25\ \mathrm{cP}$$

and from Eq. (8)

$$U_{205^\circ\mathrm{C}} = \frac{\bar{d}_p^{\,2}(\rho_s - \rho_l)g}{18 \times 1.25} f(\phi) \tag{9}$$

At any other temperature, assuming the variation in $\bar{d}_p$ and $f(\phi)$ are neglibible compared with viscosity variation, it can be shown that

$$\frac{U_{205^\circ\mathrm{C}}}{U_t} \propto \frac{\mu_t}{\mu_{205^\circ\mathrm{C}}} \tag{10}$$

A plot of $\ln(U_{205^\circ\mathrm{C}}/U_t) \propto \ln[(1/\mu_{205^\circ\mathrm{C}})/(1/\mu_t)]$ versus $1/T$ is shown in Fig. 16. Here U_t is the experimental initial settling rate at any temperature t°C, and μ_t is the calculated viscosity value from Eq. (7) at the same temperature t°C. Figure 16 illustrates that the increase in the initial settling rate with an increase in temperature is due to the decreased viscosity of the oil.

The influence of temperature on the SRC filter feed and *n*-decane system was studied at 150, 205, and 260°C with a constant *n*-decane to oil ratio of 0.25 by volume. The results are shown in Fig. 16. The nonlinear relationship between $\ln(U_{205}/U_t)$ versus $1/T$ suggests that the effect of temperature is twofold: reduction in fluid viscosity and a possible change in precipitated solid morphology and/or surface characteristics. In the case of antisolvent experiments, the interaction between the asphaltene and preasphaltene precipitates and the mineral matter at different temperatures is the dominating mechanism rather than the reduction in viscosity of the mixture. Experiments are underway to characterize the solids through filtration and subsequent benzene and pyridine washings.

CONCLUSION

The influence of various antisolvents on the initial settling rate was studied at 205°C. The initial settling rate is related to the amount of material precipitated and is correlated with a linear combination of the carbon to hydrogen ratio and the dispersion component of the solubility parameter of antisolvents. The advantage of this correlation over the ones presented earlier is that it involves the use of more fundamental and readily available properties of the antisolvent. The proposed correlation can be applied to coal-derived liquids other than SRC filter feed

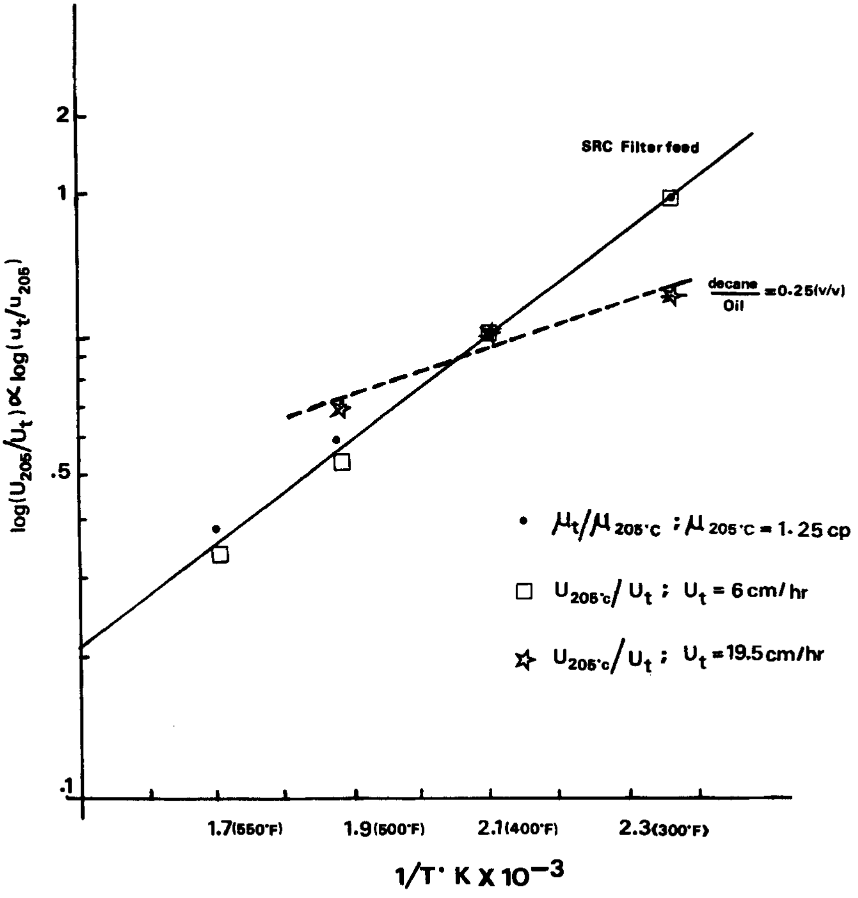

FIG. 16. Influence of temperature on the initial settling rate with and without antisolvent additions.

derived from Monterey coal and used in this study. This conclusion is arrived at because the Lummus' correlation of initial settling rate with the Watson characterization factor for the coal-derived liquid derived from Illinois #6 coal is consistent with the present results for SRC filter feed. It can be expected that the present correlation with a different set of numerical constants can be applied to other coal-derived liquids. This is yet to be tested.

The influence of antisolvent concentration on the settling rate was also studied with toluene, *n*-decane, and Soltrol-130, which confirms the fact that an increase in antisolvent dose increases the extent of precipitation and agglomeration. This also suggests that antisolvents having the lower carbon to hydrogen ratio and solubility parameter give increased sedimentation rates and are more advantageous. The influence of mixture antisolvents on the initial settling rate can be explained by their molar average carbon to hydrogen ratio and solubility parameter.

Finally, the effect of temperature on the sedimentation rate of mineral matter in SRC filter feed was studied with and without antisolvent. In the absence of antisolvent the increase in the initial settling rate is explained by the reduction in viscosity of the oil. In the presence of antisolvent the initial settling rate at different temperatures is primarily influenced by the interaction between asphaltene precipitate and mineral matter and/or precipitating different fractions at various temperatures.

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SYMBOLS

C	carbon
$\bar{d}$	average particle size, μ_m
g	acceleration due to gravity, cm/sec^2
H	hydrogen
K	kauri-butanol value
M	calculated initial settling rate, cm/hr
p, q, r	constants in Eq. (3)
t	temperature, °C
T	absolute temperature, °K
U	experimental initial settling rate, cm/hr
W	Watson characterization factor, (°R)$^{1/3}$
δ	solubility parameter
ε	dielectric constant
μ	viscosity

ρ_s density of solid
ρ_l density of liquid
ϕ volume fraction of solids

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