$K_{j,i}$ = constant characterizing the formation of the j^{th} adsorption layer by molecules of the i^{th} component

$K_{1,\beta}$, $K_{2,\beta}$ = equilibrium constants for single ($\beta = A_1, B_1$) and double ($\beta = A_1A, B_1B, A_1B, B_1A$) associates, respectively

p_i = partial pressure of the i^{th} component in a gas mixture

S = free site on the adsorbent surface

Greek Letters

ν = constant, defined for a multilayer adsorption by Equations (3) and (11)

ϵ_i = adsorption energy of the i^{th} component

$\Delta_{(m)}$ = m-dimensional region of possible variations of the adsorption energies of m components

$\Theta_{(m)}$, $\Theta^{M}_{(m)}$ = total monolayer and multilayer surface coverage for m-component gas mixture on a homogeneous surface, respectively

$\nu^{M}_{(m)}$ = multilayer surface coverage for m-component gas mixture on a heterogeneous surface

μ_i = chemical potential of the i^{th} component in the gas phase

$\mu_{j,i}$ = chemical potential of the i^{th} component in the j^{th} adsorption layer

$\Phi_{(m)j}$ = function characteristic for adsorption of m-component gas mixture and for j^{th} adsorption layer, defined by Equation (2)

$\varphi_{(m)}$, $\varphi_{(m)}^{*}$ = functions for adsorption of m-component gas mixtures, defined by Equation (16)

$\chi_{(m)}(\boldsymbol{\varepsilon})$ = m-dimensional distribution of adsorption energies

Ω_{n-1} = function; defined by Equation (4)

Vectors

$\mathbf{p}$ = $(p_1, p_2, \ldots, p_m)$, m-dimensional vector of the partial pressures

$\boldsymbol{\varepsilon}$ = $(\epsilon_1, \epsilon_2, \ldots, \epsilon_m)$, m-dimensional vector of the adsorption energies

$d\boldsymbol{\varepsilon}$ = $d\epsilon_1\, d\epsilon_2 \ldots d\epsilon_m$

Superscript

M = reference for multilayer surface coverage

Subscripts

i = component No. i

j = adsorption layer No. j

m = reference for adsorption of m-component gas mixtures

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Manuscript received November 29, 1976; revision received February 24, and accepted March 9, 1977.

Charge Characteristics of Particles in Coal Derived Liquids: Measurement and Origin

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Particles present in the reactor effluent stream of all coal liquefaction processes consist of a mixture of the original mineral matter present in coal, that is, clays, SiO_2, FeS_2, $FeCO_3$, $CaSO_4$, $CaMg(CO_3)_2$, together with unreacted and partially reacted coal residues (Walker et al., 1975). These particles range in size from 0.1 to 100 μm and constitute up to 10 wt. % of the reactor effluent stream depending on the specific process conditions. Subsequent removal of this particulate matter represents one of the major process problems associated with coal liquefaction.

This note summarizes measurements made on the sign of the charges associated with the particulate matter present in an unfiltered Solvent Refined Coal liquid having an initial 3:1 solvent to coal ratio (Wilsonville Run 94, 10-12-76, Monterey feed coal). A mechanism is presented to explain both the origin and sign of the observed charges.

EXPERIMENTS

Direct microscopic observation of particle motion in a DC electric field was used to determine the particle charge characteristics. Owing to the extremely opaque nature of the coal derived liquid, direct observations could only be made in a thin cell. The cell was constructed from a

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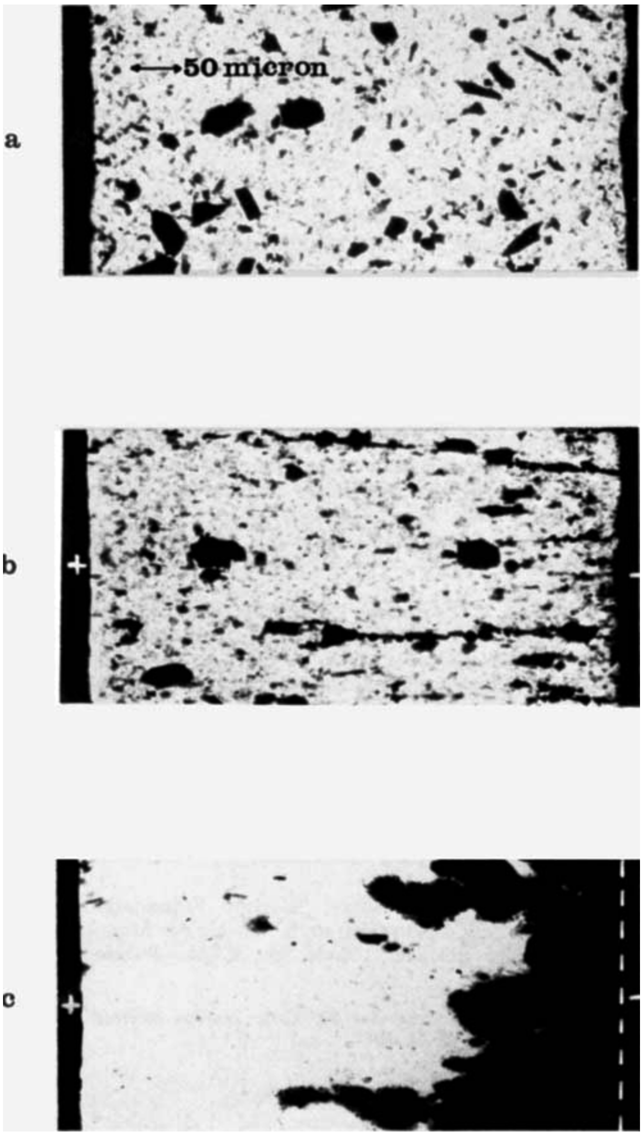

Fig. 1. Photomicrographs from thin cell arrangement (magnification 250X) of particles in 3:1 SRC filter feed. (*a*). No electric field. (*b*). 3 s after application of 100 V DC, and (c) 15 min after voltage applied.

standard glass microscope slide onto which two parallel aluminum electrodes were attached approximately 2 mm apart. A small quantity of the coal derived liquid was placed between and on top of the electrodes and a thin glass cover slide placed on top of it. The coal liquid spread to give a uniform thin film of approximately 100 μm in depth between the electrodes, in which almost all of the particles were free to move. This thin cell arrangement facilitated direct microscopic observation of the particle motion between the electrodes when connected to a 100 V AC/DC supply. However, precise measurement of particle mobility was not possible owing to electrically induced interference effects at the boundaries. In addition, a parallel plate deep cell consisting of aluminum electrodes 7.5 × 2.5 cm suspended 2 mm apart was used to eliminate edge effects and to examine the electrophoretic deposition of particles.

OBSERVATIONS

A photomicrograph of the particulate matter randomly orientated and distributed in the thin liquid film between the electrodes is shown in Figure 1 *a*. Application of the electric field resulted in a reorientation of almost all of the observable particles such that their major axes were positioned along the electric lines of force. The larger particles were then seen to migrate along the force lines towards the negative electrode. Simultaneously, they formed long chainlike structures, as shown in Figure 1 *b*. These larger particles and chain structures were seen to migrate towards the negative electrode with appreciably higher velocities than the smaller particles. Approximately 15 s after application of the electric field, almost all of the larger particles had collected at the negative electrode where they remained oriented along the lines of force. These observations permit an order of magnitude estimate of 1×10^{-5} cm/s/V/cm for the mobility of the larger particles. This value is of the same order as those obtained by van der Minne and Hermanie (1952, 1953) using more precise measurement techniques for the electrophoretic mobility of charged carbon particles in nonaqueous media.

The collection of the larger particles at the negative electrode is accompanied by the gradual appearance of a particle free zone adjacent to the positive electrode, formed as a result of uniform migration of the smaller particles. After approximately 15 min., with an imposed voltage of 100 V, almost all of the particles have collected at the negative electrode, giving quantitative removal of the particulate matter from the coal derived liquid. This leads to the conclusion that the particles carry a net positive surface charge. A photomicrograph showing this final condition is presented in Figure 1 *c*. Reversal of polarity at the electrodes resulted in almost total removal of the collected solids which then migrated towards the opposite electrode. The application of an AC field at equivalent voltage produced no observable migration of particles. The particles did, however, reorientate to align with the electric force lines.

Inspection of the electrodes removed from the deep cell after imposing a DC voltage of 100 V for 30 min clearly showed only the negative electrode to be completely coated with a thick black deposit. Rodgers (1976) and Briggs (1976) conducted similar experiments but did not observe the uniformity of charge found in this investigation. This could be due to a combination of different coal liquid samples and experimental conditions. Artifacts were observed in our experiments when the voltage gradients were not in the range 100-1000 volts/cm.

DISCUSSION

The observed electrokinetic phenomena of the particulate matter present in coal derived liquids can be explained by the combined phenomena of electrophoresis and dielectrophoresis. The criteria for electrophoresis as stated by van der Minne and Hermanie (1952) are: the motion of the particles should be rectilinear, unidirectional, and uniform between electrodes; the velocity should be independent of the position in the electric field; and the velocity should be proportional to the field strength, independent of particle size, and should reverse on reversal of the field. In contrast, dielectrophoresis is characterized by dielectric polarization of particles due to nonuniform electric field which can lead to chain formation; the motion of the particles is nonuniform, and the particle velocity is proportional to the second power of both the electric field and particle size.

The fact that all of the particles migrate in one direction, carrying a net positive charge, indicates that electrophoresis is occurring. On the other hand, the chain formation and higher mobility of the larger particles are indicative of dielectrophoresis.

The particles reversed direction on reversal of DC polarity and did not migrate in an AC field. Hence, it can be concluded that the observed particle mobility was due primarily to the electrophoresis of positively charged particles. Dielectric polarization undoubtedly occurs, as evidenced by the chain formation. Dielectrophoresis has only a second-order effect, since there was no observable difference in mobility on reversal of polarity. The negligible mobility in an AC field also supports this.

ORIGIN OF POSITIVE CHARGE

The above discussion satisfactorily explains the observed electrokinetic phenomena occurring in the thin cell apparatus, but perhaps the most significant observation is that almost all the particles carry a positive charge. This is somewhat surprising when we consider the differences in chemical composition of the individual particles present in coal derived liquids.

The exact chemical composition of coal derived liquids is unknown and is currently the subject of considerable research (Farcasiu et al., 1976). Sternberg (1976) and Farcasiu et al. (1976) have identified preasphaltenes, asphaltenes, and oil as the three major constituents of coal derived liquids. Preasphaltenes and asphaltenes invariably constitute more than 60% of the final coal derived liquid product. Sternberg et al. (1975) have proposed an acid-base structure for coal derived asphaltenes, in which complex formation occurs by hydrogen bonding between acidic phenol and basic nitrogen groups. Furthermore, Sternberg (1976) suggests that the preasphaltenes and even the parent coal may have a similar type of structure. Burk and Kutta (1976) report that preasphaltenes exist as saltlike species and contain up to 80% of the basic nitrogen present in the coal liquid.

Investigations into the charge carrying characteristics of asphaltenes have been confined to those derived from crude oil. Csayni and Bassi (1958) showed that petroleum asphaltenes carried either a positive or negative charge, depending on the origin of the crude oil. Wright and Minesinger (1963) demonstrated that asphaltenes in nitrobenzene carried a positive charge.

In view of the available evidence on the charge carrying characteristics of asphaltenes, it is very likely that these compounds, or some derivative, could provide the observed positive charge on the particles. Futhermore, there is evidence (Henry et al., 1976) to show that the particles present in coal derived liquids acquire an adsorbed surface layer of asphaltene/preasphaltene material.

A possible mechanism explaining why the particles acquire net positive rather than negative or neutral surfaces can be deduced from the acid base model of asphaltenes and preasphaltenes. During the initial stages of coal liquefaction, hydrogen donor solvent is utilized at elevated temperature and pressure. Under these conditions, the preasphaltenes and asphaltenes are solubilized by rupture of the hydrogen bonds between acidic and basic groups. Breakage of the hydrogen bond does not by itself confer a net charge on either the acidic or basic group. However, the ring nitrogen present in the basic group possesses free electrons and will attract protons present in solution in the hydrogen donor solvent. Hence, the basic component of asphaltene acquires a net positive charge. These new ionic species will be attracted to any solid surface having a higher dielectric constant than the surrounding liquid. Electrical neutrality is maintained since the negative counter ions remain in solution, forming a diffuse electrical double layer around the particles.

This mechanism of particle charging is supported by experimental observation of the effect of quinoline addition to suspensions of particulate matter in a hydrogen doner solvent. Quinoline contains a ring nitrogen similar to the basic group present in asphaltene. Particulate matter filtered from a coal derived liquid and benzene washed to remove asphaltenes was resuspended in a hydrogen doner solvent, anthracene oil. The addition of a small amount of quinoline resulted in a considerable increase in mobility of the particles towards the negative electrode. The addition of quinoline to a suspension of otherwise immobile clay particles in anthracene oil resulted in a similar effect.

CONCLUSION

The experimental investigation outlined in this note shows that the particulate matter present in coal derived liquids exhibit appreciable electrophoretic mobility due to a net positive surface charge. The origin of the positive charge is explained in terms of the acid base structure of asphaltic species and the presence of protons in the coal derived liquid. Corrobarative experiments using quinoline to model the basic component of coal derived asphaltenes confirm that a positive charge is conferred to particulate matter suspended in a hydrogen doner solvent. An understanding of the sign and origin of the charge on particles in coal derived liquids should be of considerable interest to researchers currently investigating the feasibility of techniques such as flocculation, electrically induced separations, and interfacial collection or distribution to water for the removal of the particles. Studies are currently in progress in our laboratory on all of these techniques.

ACKNOWLEDGMENT

The authors are indebted to the Energy Research and Development Agency for financial support of this work under grant E(40-1)-5105 and to Dr. H. W. Sternberg for useful discussions relating to the origin of the charge on the particulate matter.

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Manuscript received March 15, and accepted March 30, 1977.