

THE ELECTROPHORETIC MOBILITY DISTRIBUTION IN AQUEOUS DISPERSIONS OF BITUMINOUS COAL AND RESIDUAL HYDROCARBON MATERIALS

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INTRODUCTION

The effect of mineral content on the electrokinetics of coal is very pronounced and contributes to a more hydrophilic surface that contains a substantial quantity of bound water. Mineral composition is known to vary markedly from coal to coal as does water content. Dewatering is an important aspect of coal preparation (1). In addition, there is evidence that the native mineral residue in coal plays an important catalytic role in direct hydro-liquifaction.

All of the above can be related to the electrophoretic behavior of the coal surface which in turn depends on the surface functional groups present. Even though intrinsic heterogeneity in coal produces no single and universal structure, enough similarity exists in those functionalities to predict the surface charging mechanisms. Previous explanation for surface charging on coal, based on oxide-like hydration and dissociation, fail to explain the positive charge at low pH so that the surface functionalities involved must include more than simple oxide groups.

These ideas were extended to the surface chemistry of residual hydrocarbon materials, the unconverted vacuum bottoms (uvb), obtained in petroleum refining. The uvb products are an unknown material that may have an asphaltene character, but the test is not conclusive. A significant result of this work was the finding that the electrophoretic properties of the uvb products resemble bituminous coal.

Coal fines and uvb products have not been commercially successful materials in the past. Recent efforts in coal-oil and coal-water systems, utilizing pulverized coal, have been promising. A similar role may be foreseen for the uvb products in slurry form.

In this paper, we report the full electrophoretic mobility distribution for several bituminous coals and a friable uvb sample as a function of pH in aqueous media. A discussion of the main structural features that effect electrophoresis is presented. The key parameters include determination of heteroatoms, carbon framework, mineral matter and physical structure, especially pores.

EXPERIMENTAL

Materials

The bituminous coal samples were kindly supplied by the Atlantic Research Corporation of Alexandria, Virginia, USA, and were studied along with a reference sample obtained from the General Motors Corporation that had been extensively studied in earlier work (2-5). All samples have been ground in the dry state and then sieved, as designated in Table 1. The ash content was determined by the University of Massachusetts Microanalysis Laboratory at 1000°C in oxygen and also reported in Table 1. The coal was stored in closed containers until used.

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The Chyoda sample, an unconverted vacuum bottoms residue, was obtained from Japan and supplied by KSE, Inc. of Amherst, Massachusetts. The initial condition was 0.5 centimeter friable black lumps. Samples were ground by hand in a mortar and pestle and then sieved dry, 100% -200 mesh. An elemental analysis was determined at the University Microanalysis Laboratory and is reported in Table 2. The percentages are in quantitative agreement with the elemental analysis generally found in these materials (7).

The water was distilled a second time from the in-house supply in a Corning AG-1b all Pyrex still. Certified ACS grade NaOH and HCl were obtained from Fisher Chemical Company.

Sample Preparation

A stock slurry was made by adding one gram of powder to 20 ml of twice distilled water. This was then mixed continuously on a stirring plate at medium speed for 48 hours at room temperature (23-25°C). The Chyoda sample was stirred for 72 hours at the same temperature.

Clean polyethylene containers (Nalgene LPE) were partly filled with 50 ml of distilled water and the pH adjusted to a preliminary value using KOH or HCl respectively. Ten drops of the stock coal slurry were then added to the bottles containing the water of known pH, giving a volumetric dilution factor of approximately 1/200.

The samples were then stirred on a stirring plate for 3 minutes at fast speed and then allowed to settle overnight at 30°C. After equilibration, the pH of the supernatant was taken, the mixture stirred at medium speed for two minutes, and the mobility then measured.

Microelectrophoresis

Electrophoretic mobility was measured with a Pen Kem 3000 automated electrokinetics analyzer (8). The instrument has a silica sample chamber with permanently bonded palladium electrodes. Particles are illuminated with a 2mW He-Ne laser and their image is projected onto the surface of a rotating radial grating. Electrophoretic movement causes a frequency shift in the light transmitted through the grating as compared to a reference detector. A fast Fourier transform analyzer computes the frequency spectrum from the individual contributions of the light scattered from many particles in order to obtain a representation of the electrophoretic mobility distribution. Focusing at the stationary layer is under automatic control. Measurements were made at both front and back stationary layers, under computer control, and the results averaged to ensure maximum accuracy.

RESULTS

In Figure 1 we show the distribution of the electrophoretic mobility for GM coal C8 at selected pH over the range studied. The pronounced features, multiple peaks and variation in peak breadth, were also observed in the other coal samples. In Figure 2 we show the dependence of the electrophoretic mobility distribution on pH for the Chyoda uvb C27 sample. The general features, multiple peaks and variation in peak breadth are shown by the Chyoda sample as well.

The average mobility as computed by the Pen Kem 3000 is shown as a function of pH shift from the isoelectric point (iep) for all four samples in Figure 3. The iep's for the coals were 6.0, 6.2, and 6.4, somewhat lower than 6.8, the iep of the Chyoda uvb sample. The curves reflect the specific nature of each sample within a similar overall envelope and a trend that shows extrema in mobility at low and high pH.

DISCUSSION

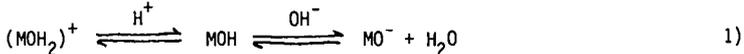
Multimodal Distribution

GM coal had a multimodal distribution, shown in Figure 1, which suggested the presence of a major second component such as a mineral oxide. The effect of polydispersity in size, although a complicating factor, cannot explain the wide differences in electrophoretic mobility of the individual peaks. For example, at a pH of 6.65, the emd peaks occurred at a mobility of -2.2, -0.9, -0.4 and +0.1 ($\mu\text{m/s})/(\text{V/cm})$ respectively. The differences observed here are far larger than the 50 percent mobility variation expected between the Hückel and Smoluchowski limits at a given zeta potential. In addition, since there is a continuous distribution in size as verified in photomicrographs, separate peaks would not be expected to occur. It is interesting to note that the individual peaks appeared to be reproducible over a wide pH range and individual peaks widened away from the iep in a similar manner to the other coals studied in this work. Statistical variation in sampling plus a small amount of flocculation near the iep could have had some effect on the emd.

AMPHOTERIC BEHAVIOR

The hydrogen and hydroxyl ions were found to cause amphoteric behavior in all samples measured as shown in Figures 1-3. This observation is in agreement with the conclusions of Fuerstenau et. al. (9), who observed amphoteric behavior in both native and demineralized coal samples.

Amphoteric behavior is caused by dissociation of a single surface group,



where M represents a metal ion, or, in the case where there are two distinct functional groups present, one that accepts a proton to become positively charged and one that dissociates and leaves a negative site. The zwitterionic surface is common in biological systems where the two groups responsible are usually the carboxylic and the amino groups.

The change in zeta potential (derivable from the mobility) with pH, $d\zeta/d\text{pH}$, at the isoelectric point (iep) gives an indication of how closely H^+ and OH^- can be considered potential determining ions. It is assumed here that the surface potential is close to the potential at the surface of shear, near the iep. Addition of acid or base will alter the chemistry of the solid, creating irreversible effects, which causes deviation from the ideal Nernstian behavior of 59.2 mv/pH unit at 25°C (10).

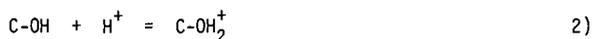
Smith (11-13) has shown that deviations from the ideal Nernst equation become important when the fraction of sites ionized at the point of zero charge is small. Under these conditions the Nernstian slope is reduced by a factor equal to $\ln(\theta_+/ \theta_-)$, where θ is the fraction of sites of given charge that are ionized at the iep. The iep is then characteristic of an absence of charge rather than an equal number of positively and negatively charged sites.

All coals measured in this work had slopes roughly one half of the Nernstian value. The simple oxide, alpha alumina, reported elsewhere (14), had a slope similar to the coal samples. The uvb had a much lower slope, indicating that a small amount of charge was present at the iep. This suggests that the surface charging on coals used here behaved more like an oxide than a hydrophilic carbon. Fuerstenau (9) has demonstrated the importance of using low ash coal in order to avoid measuring an oxide rather than a coal surface. It is interesting to note the significant rise in mobility at the extremes of pH for the uvb sample. This can be interpreted as ionization of heteroatoms at high and low pH values, leaving little or no ionization at the iep. Zwitterionic surfaces such as these were shown to be expected to depart markedly from Nernstian behavior as discussed by Hunter (15).

The interpretation of the dependence of the breadth of the distribution on pH has been given in an earlier paper (16). Increased ionization at larger pH shift from the iep produces a wider spectrum in the electrophoretic mobility distribution.

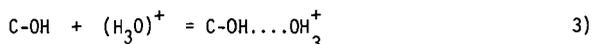
Several authors have proposed that the principal charge bearing groups on demineralized coal were oxygen functionalities such as aromatic alcohols (phenolic) and carboxylic acids (9,17). If these groups were alone responsible for surface charge on coal, hydrolysis in water would cause the donation of protons to water, the weaker Brönsted acid, creating only negative charge. Amphoteric behavior would not be observed. This is predicted by the theoretical work of Healy and White (18).

Attempts to explain the positive surface of coal by the following charging mechanism (19),



are based on the unsupported hypothesis that the adsorbed proton bears the positive charge. The origin of this concept lies in the attempt to compare the charging mechanism on coal to the metal oxides such as AlO. Protonation of a metallic hydroxide, MOH, produces a coordinated water molecule which gives an unbalanced and positive formal charge to the metal ion as, M:OH. The hydrogen atoms of water do not bear the charge. This is supported by the fact that charge on a hydrated metal ion in solution resides on the ion and not on any protons of the coordinated water molecules (20). Carbon, which is unable to coordinate water molecules, cannot give rise to positive charge in this manner.

We propose an alternative mechanism giving a positive charge through hydrogen bonding of an hydronium ion.



The decrease in mobility giving maxima at both high and low pH follows as a consequence of increased screening at high ionic strength.

In addition, most coals have mineral matter incorporated into their structures in various degrees. These are classified into three categories, 1) admixed minerals of larger size, 2) incorporated minerals as a result of metamorphic processes and 3) inherent minerals uniformly distributed within the organic matrix (21, 22). Demineralization procedures probably do not remove all of the mineral matter. For example, treated coal had as much as 10 percent of the ash content of untreated samples in Fuerstenau's work (9). Table 1 shows the ash content of untreated coals used in this work. The degree of entrapment determines how easily coal can be cleaned and is of current interest in beneficiation.

The extensive pore structure of coal will contain embedded water with dissolved salts, minerals, humic acids and organic matter. The release and subsequent adsorption of various species from these pores is likely to be a function of pH. One of the techniques used to determine the moisture retention and pore structure is to observe the behavior of metallic ion adsorption on coal (23).

Such selectivity will allow the transport of only certain materials into and out of those pores, analogous to a molecular sieve. Evidence for this behavior is shown in Figure 3, where the average mobility for several samples is plotted as a function of pH units away from the iep. Two features can be noted: first, the maximum negative mobilities are all similar in value, and secondly, the maximum positive mobilities have a larger amount of variation.

We interpret the above as follows: at high pH, the carboxylic and phenolic groups on the carbon skeleton of coal are mainly responsible for the negative charge. The organic framework is basically similar for the fully oxidized surfaces in this work and will result in similar electrophoretic mobility. This interpretation is supported by recent results obtained by Sequential Elution by Specific Solvents Chromatography, SESC (24). Findings indicated that although different coals varied greatly in overall structure, many of the same chemical groups were always present.

At low pH, positive functionalities, metallic oxides and adsorption of metal ions leached from pores all contribute to the observed mobility. The larger amount of variability expected in these processes will be reflected in a greater difference in the mobility that is observed from sample to sample.

This is in agreement with the results of Wen and Sun (25) who showed that at

lower pH, the zeta potential of oxidized coal was controlled by the presence of electrolytes such as Fe^{+2} and Al^{+3} ; both of which form hydroxides at pH values below 8. Above this pH, the metal ions behaved much like an indifferent electrolyte with little or no effect on the zeta potential. In addition, they also suggested that variations due to oxidation, shown to be small above pH 7 as compared to larger variation below pH 7, might be explainable due to the solubility of humic acids on the coal surface.

It is important to note that the measurements will be very sensitive to the solids concentration of the slurry. Previous workers have not specified this important parameter. In addition, the aging effects will be most pronounced in the high concentration region. Conditioning and aging procedures are generally not reported in the literature either. In this work, care was taken to properly condition a dilute stock solution for three days followed by further dilution to a very low particle concentration at a given pH in order to avoid any high concentration anomalies. By avoiding excessive leaching of inorganic ions, we are seeing the electrophoretic mobility of the coal surface and not a layer on inorganic hydrolysis precipitate. This could account for the generally high iep observed in this work as compared to other values in the literature (9, 25).

The composition of the uvb sample, while not completely understood, appears to consist of condensed polynuclear ring systems which have alkyl side chains containing heteroatoms such as nitrogen, oxygen and sulfur (7). Limited data suggests that oxygen is present as non-hydrogen bonded phenolic groups.

The concentration of mineral oxide in the uvb material is very low; it was found to be 0.9 percent for the sample reported in this work. The observed amphoteric behavior may then be explainable in terms of zwitterionic surface groups. It the uvb materials are really primarily asphaltenes, then this is in agreement with the conclusions of Cratin, who has suggested that the amphoteric nature of the asphaltenes might be similar to amino acids (26).

ACKNOWLEDGEMENTS

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Table 1. Ash Content and Sieve Fractions

<u>Sample (#)</u>	<u>% Ash*</u>	<u>Sieve mesh</u>
Island Creek (c26)	16.0	200 x 325
Gen. Motors (c8)	4.8	-200
Bishop (c28)	4.7	200 x 325
Chyoda uvb (c27)	0.9	-200

*Determined by the University of Massachusetts Microanalysis Laboratory at 1000°C in oxygen.

Table 2. Elemental Analysis* of Chyoda uvb

<u>Element</u>	<u>Weight %</u>
Carbon	86.5
Hydrogen	6.0
Nitrogen	1.5
Sulfur	5.3
Oxygen	0.7

*Determined by the University of Massachusetts Microanalysis Laboratory.

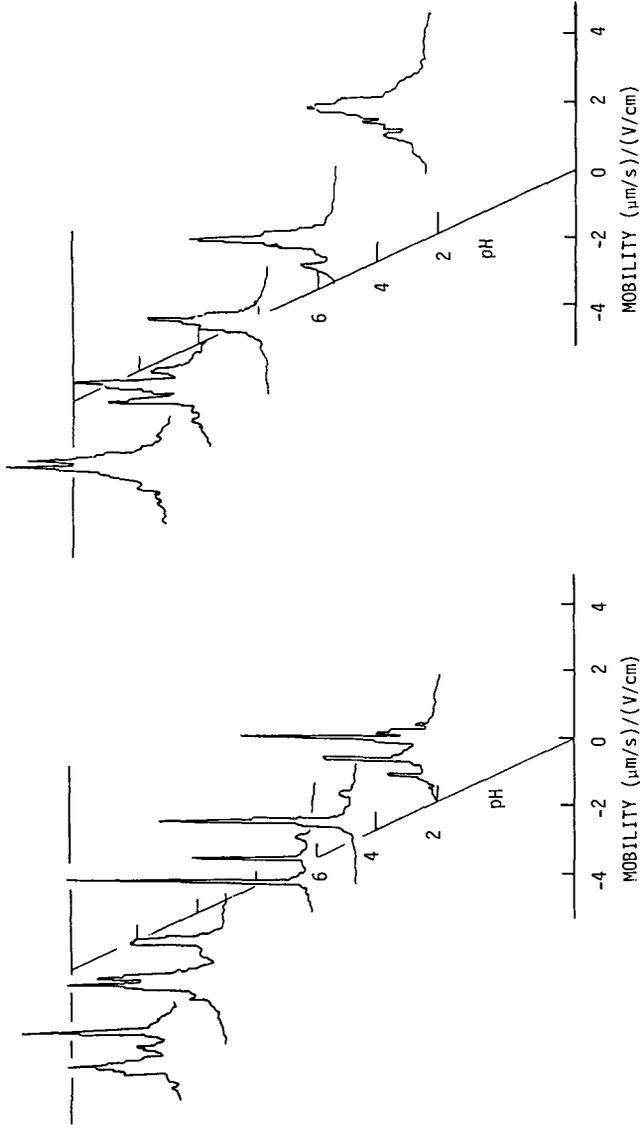


Figure 1. Electrophoretic mobility distribution as a function of pH for General Motors coal sample C8.

Figure 2. Electrophoretic mobility distribution as a function of pH for Chiyoda uvb sample C27.

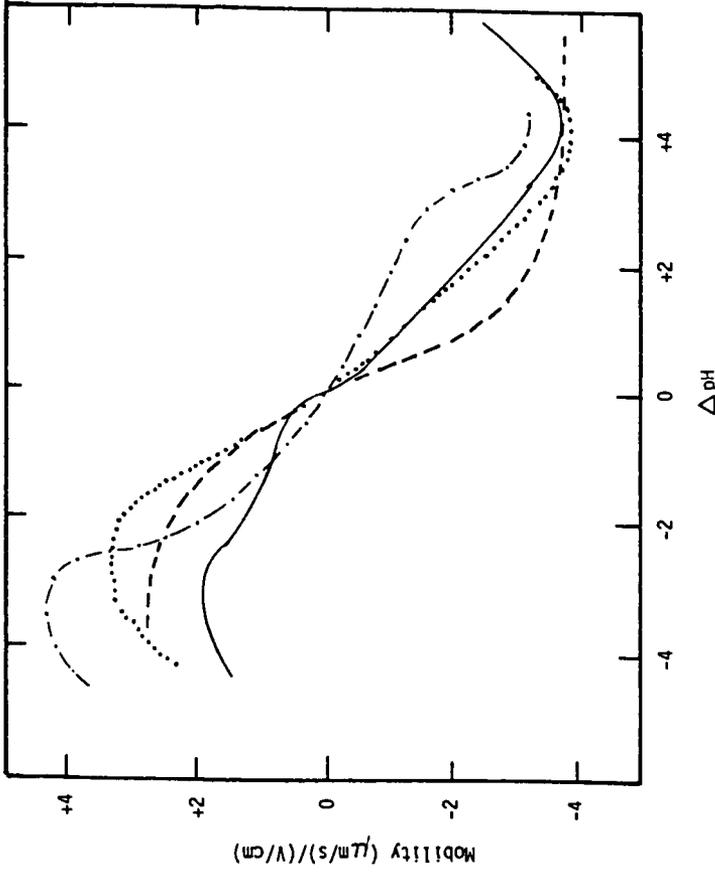


Figure 3. Average electrophoretic mobility as a function of pH shift from the isoelectric point for unconverted vacuum bottoms (uvb) and several coals. Samples (and isoelectric points) are: solid line, General Motors coal C8 (6.0); dashed line, Bishop coal C28 (6.4); dotted line, Island Creek coal C26 (6.2); and dash/dotted lines, Chyoda uvb C27 (6.8).