

**COAL ELECTROKINETICS: THE ORIGIN OF CHARGE AT
COAL/WATER INTERFACE**

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Introduction

Electrokinetic measurements provide valuable information on the properties of coal aqueous suspensions that depend on the charge of the particles; examples include coal particles floatability, coal suspensions stability and rheology, coal fines filtrability, etc. Such measurements reveal the relationship of charge to the nature of coal and how the charge is effected by the liquid phase composition. It may also serve as an additional tool in the studies on coal surface composition.

For any solid/liquid system both the composition of the solid and the concentration and valency of ions in the solution contribute to the sign and value of the electrokinetic potential. In the case of very dilute suspensions containing a small number of individual particles in a large amount of solution, as in microelectrophoretic experiment, the contribution from the value of surface potential is more important. For the concentrated suspensions, however, as in the case of electrophoretic mass transfer experiment, the value of the zeta potential, depends to a large extent, on the concentration of ions in the liquid phase.

The results discussed in this paper all pertain to the conditions of conventional microelectrophoretic experiment conducted at extremely low solid concentration.

Recent analysis of the available data on electrokinetics of coal/water suspensions [1] has led to a general relationship (Fig. 1) which shows schematically the microelectrophoretic mobility - pH curves for the coals of different rank. The shift of the curves for lower rank coals towards more acidic pH ranges resembles the shift caused by oxidation [2].

As seen from Fig. 1, the zeta potential - pH curves for coals clearly exhibit iso-electric points; thus coal particles have both negative and positive sites.

Coal particles are extremely heterogenous: various heteroatoms and functional groups along with inorganic impurities are present in the hydrocarbon matrix. These surface sites exhibit various electrochemical characteristics and they all contribute to the overall electrical surface charge of coal particles. The basic concept of this paper is that under the conditions of a microelectrophoretic experiment, in which small number of solid particles is suspended in a large volume of solution, there are three main effects contributing to the surface charge of coal particles:

- (i) coal hydrocarbon matrix,
- (ii) coal heteroatoms and functional groups,
- (iii) coal inorganic impurities.

In experiments at higher solid/solution ratio, a fourth effect, the effect of dissolved species, may play a more important role in determining surface charge.

Model Systems

Hydrocarbons. Fig. 2 shows Mehrishi and Seaman's [3] data obtained for anionic (RCOOH), nonionic (ROH) and cationic (RNH₂) hydrocarbons. The electrophoretic mobility versus pH curves confirm the presence of carboxyl group for the acid with pK estimated to be about 4.3, as the pH at which the microelectrophoretic mobility is one-half of the plateau value, similarly for n-octadecylamine pK is 8.8. The

electrophoretic mobility curve for the non-ionogenic but polar compound, octadecanol, reveals that this hydrocarbon is negatively charged over the whole pH range. Hollinshead et al. found [4], however, that the purified octadecanol showed lower electrophoretic mobility which may suggest the influence of trace contaminants.

Nujol (medical paraffin) droplets in water were shown by many researchers to be negatively charged over the whole pH range [5,6]. This is consistent with Wen and Sun's results obtained for six hydrocarbons between hexane to octadecane [7] (Fig. 3). Droplets of kerosene in water are also negatively charged over the entire pH range [7,8]. It is of interest to observe that Perreira and Schulman [9] found that pure paraffin wax was negatively charged above pH 5. The zeta potential values for paraffin wax reported by Arbiter et al. [10] were negative in the pH range 3 to 10.

Our measurements with aromatic hydrocarbon, anthracene (Aldrich, purity 98%+), show similar mobility-pH relationship: anthracene crystals are negatively charged over the whole pH range. It seems then that the H^+ and OH^- ions play predominant role in charging a neutral hydrocarbon wall.

Nujol oil droplets with adsorbed polysaccharide molecules, containing no acidic or basic groups, were found not to acquire any charge [5].

Such results as received above suggest that while the effect of ionic groups can be satisfactorily predicted, the contribution of the hydrocarbon matrix to the overall particle charge needs to be reexamined.

Graphite. Spurny and Dobias [11] reported that pure Ceylon graphite was negatively charged in aqueous solution, with the zeta potential increasing continuously over the pH range 2 to 10. Similar results were obtained by Chander et al [12].

Fig. 4 shows our results obtained for Ceylon graphite [13]. In our experiments, an original finely ground graphite sample, as well as sample purified by leaching were utilized in microelectrophoretic experiments. The leached sample was prepared by conditioning 10 g of finely ground graphite (below 38 μ m) in 100 ml of 1 N HCl solution at 45°C for 16 hours, followed by filtration, thorough washing with distilled water and drying at 50°C. 62 ppm Fe, 12 ppm Al, 9 ppm Mg and 17 ppm Ca were detected in the pregnant solution. ICP analysis of the original sample revealed the following major impurities: 0.14% Fe, 0.02% Ca, 0.01% Mg, 0.01% Ti, 0.01% Al, 0.01% Na, 0.01% K and 0.01% P. All other impurities present in the sample assayed less than 50 ppm. Examination of both samples under a scanning microscope (ETEC, Autoscan) gave no indication of alterations of the mineralogical structure introduced by the leaching. Specific surface area measurements carried out with the use of a Quantsorb (Quantachrome Corp.) apparatus and nitrogen gave 5.08 and 5.25 m^2/g for the original and leached -38 μ m graphite samples, respectively.

As it can be seen from Fig. 4, both graphite samples exhibit negative zeta potential values over the whole pH range. The leached sample is more negative points to the role the cationic surface centers like Fe^{3+} , Ca^{2+} and Mg^{2+} may play.

Graphite particles which are handled in air are claimed to be partially oxidized [14] which probably explains the graphite particles behavior in the electrokinetic experiments.

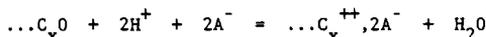
Carbon Black. Carbon black is a form of elemental carbon prepared by partial combustion of various carbon-containing substances (cone sugar, liquid or gaseous hydrocarbons, etc). They contain above 90% carbon, with oxygen and hydrogen being the other two major constituents [15]. Carbon blacks can be graphitized by heating in the absence of oxygen. This process leads to the elimination of functional groups and growth of graphitic layers. High temperature treatment (up to 3000 °C) provides a solid structure closely resembling that of graphite [16].

The origin of charge on carbon black particles has attracted the attention of many researchers. Miller [17,18] studied adsorption from aqueous solutions on the charcoal prepared from purified cane sugar by prolonged heating at 1200 °C followed by activating heating for 24 to 48 hrs at the same temperature in the presence of a

limited supply of air. Such a charcoal was found in the adsorption studies to cause decomposition of neutral salts with the base set free and the equivalent amount of acid adsorbed onto charcoal. The process is referred to as hydrolytic adsorption. Frumkin and his co-workers [19,20,21] showed that carbons outgassed at 950 °C did not adsorb mineral acid from a dilute solution and that adsorption could be restored in the presence of oxygen. They also found an exponential relationship between the oxygen pressure and the acid adsorption. In Frumkin's electrochemical theory the oxygen adsorbed on carbon surface is assumed to ionize to some extent with the formation of hydroxyl ions; the carbon surface acquires positive sign in this process and the solution becomes more alkaline:

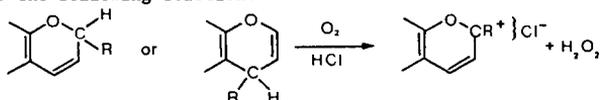


where $\dots C_x O, 2A^-$ stands for positively charged carbon surface with adsorbed anions. In acidic solution

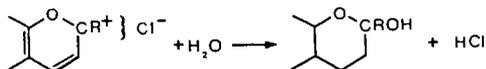


The carbon then acquires positive charge in the presence of oxygen [22,23,24], but the same carbon exposed to oxygen for long periods, or at elevated temperatures, oxidizes and dissociation of the oxygen functional groups imposes a negative charge on the system in an aqueous environment [25,26].

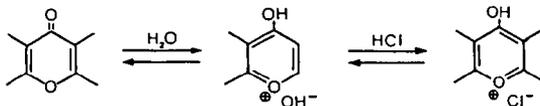
Garten and Weiss [27] postulated that the carbons contain chromene structures. A characteristic reaction of this group is the formation of a carbonium ion according to the following reaction:



The benzopyrylium(carbonium) ion is a weak base having a dissociation constant of the order of 10^{-10}



Garten and Weiss [27] pointed out that chromene structures on the surface of an H-carbon would function as a redox system. In the presence of oxygen and acid the carbon is oxidized so that it acquires the potential of the oxygen-hydrogen peroxide couple with which it is in equilibrium, and, hence, the adsorption of acid anions at the carbonium ion sites is a function of the oxygen partial pressure and the pH value of the solution. This chromene-carbonium ion couple may then be regarded as a chemical background for Frumkin's electrochemical theory.



Voll and Boehm [28] found evidence for a different cyclic ether structure, pyrone-like structure, characterized by basic properties. According to them each basic site contains two oxygen atoms, but they may be located in two different rings of a graphitic layer.

Arbiter et al [10] came to a conclusion that for hydrophobic solids, the double layer is entirely on the water side of the interface and is then analogous to that at the water/air interface. James in his review [29] showed a straight line

which approximates the experimental curve for Nujol as a typical mobility versus pH relationship for a nonionogenic surface.

Coal Electrokinetics

Coal is heterogenous at a number of levels [30]. At the simplest level it is a mixture of organic and inorganic phases, but because mineral matter originated from the inorganic constituents of the precursor plant organic materials (syngenetic mineral matter), and from the inorganic components transported to the coal bed (epigenetic and epiclastic mineral matter [31]), its textures and liberation characteristics differ. Mineral matter may occur as deposits in the cracks and cleats, but also in the form of very finely disseminated discrete mineral particles. Coal also contains inorganic matter in the form of chemically-bonded elements (such as organic sulfur and nitrogen).

The most important common coal minerals include [32]: clay minerals (kaolinite, illite), silicates (quartz), carbonates (dolomite, siderite), disulfides (pyrite, marcasite), sulfates (gypsum), and sulfides (galena, pyrrhotite). Aluminosilicates make up as much as 50% of the total mineral matter content, and quartz usually accounts for up to 20% of all mineral content.

Physical separation of mineral matter from coal depends mainly on its uniformity of distribution. Epigenetic minerals, which are typically concentrated along cleats are preferentially exposed during breaking of coal and thus are physically separable from coal.

Recent findings indicate that most of the mineral matter included in coal to the micron particle size range is a distinct separable phase which can be liberated by crushing and very fine grinding. Separation of coal particles from such a liberated gangue can lead to clean coal concentrate containing about 1% of ash [33]. Usually cleaned coal contains 6-8% ash. Cleaned coal has then considerably reduced the content of silicates, carbonates, disulfides and sulfates, but still contains various chemically bonded inorganic elements as well as finely disseminated minerals incorporated in the hydrocarbon matrix. In one of the first papers on coal electrokinetics, Sun and Campbell [34] demonstrated that the zeta potential versus pH curves are very sensitive to inorganic impurities content.

The coal minerals have very different electrokinetic characteristics. Aluminosilicates develop negative charge at basal planes as a result of isomorphic substitution, but the edges are characterized by $pH_{i.e.p.} = 9.1$, as for Al_2O_3 .

Quartz is negatively charged practically over entire pH range, while i.e.p. of dolomite and calcite is claimed to be situated in the slightly alkaline pH range.

Fig. 5 shows that for some coals demineralization by leaching, which in this particular case decreased ash content from about 11% to below 1%, can alter coal electrokinetic properties very significantly [35]. Apparently not only the content of ash but also its chemical composition must be important. It is therefore very doubtful whether the empirical equation that interrelates the zeta potential value with the coal chemical composition, and among other factors the ash content, as recently was proposed by Mori et al [36], can reflect true effect of the inorganic matter on the coal zeta potential.

Fig. 6 reveals one of typical problems facing researchers in the area of fine coal beneficiation [37]. While upper curves were obtained with the use of fresh fine material produced by crushing coarser pieces selected manually from the investigated coal samples, the bottom curve shows the zeta potential values for the same three coal samples which, however, were not produced by crushing coarser lumps, but rather by sieving the samples. In the latter case the experimental points for all three samples practically lay on the same zeta potential pH curve. This curve is not very different from the one obtained for precipitated humic acid (purified Aldrich sodium salt of humic acid was used). This interesting result, although not discussed here, shows again how misleading results can be produced in this area.

The Charge at Coal/Water Interface

Coalification and coal rank are synonymous with progressive enrichment of coal in organically bonded carbon.

Coal is a highly crosslinked polymer, which consists of a number of stable fragments connected by relatively weak crosslinks. The average number molecular weight per cross link increases with the rank of coal and that can be ascribed to the presence of larger molecules assembled together to form the macromolecules or to fewer cross links in higher rank coals. The aromatic carbon content, which is about 50% for subbituminous coals, increases to over 90% for anthracite [38].

Electrochemical properties of the coal/aqueous interface are mainly determined by coal functional groups and heteroatoms. Therefore, the effect of oxidation on coal electrokinetic potential as reported by many researchers [39,40,41,42], is very consistent. The content of phenolic groups decreases gradually with increasing coal rank [43], while carboxylic groups are of little importance in coals with greater than 80% carbon content [44,45]. The zeta potential versus pH curves for low rank coals can be approximated with two straight lines, while for fresh high rank coals the same relationship can be approximated with a single line (Fig. 1). The former indicates that the oxidized coal contains various acidic groups, while the latter behaves similarly to a nonionogenic solid as already discussed. It is likely that oxidized coal contains not only carboxylic groups with $pK = 4.7$ as for carboxylic acids, but probably also more acidic carboxyls, as for instance the carboxylic groups in position ortho to phenolic hydroxyl (for such carboxyls, as in salicylic acid, $pK = 3.0$).

Another important heteroatom, sulfur, appears in three forms: organic sulfur, pyritic sulfur and sulphatic sulfur. Sulfate sulfur is usually of only minor importance and occurs mainly as gypsum which is to a large extent removed in physical cleaning of coal. The same physical separation removes only coarse pyrite leaving with coal finely disseminated pyrite.

Some researchers found [46] that when pyrite is present in the coal in high concentrations, its oxidation products control the surface charge on coal particles. What is then the origin of the electrical charge at a coal/water interface?

There is no doubt that negative sites on coal surface are provided by carboxylic and phenolic groups (Fig. 7), and also by inorganic impurities such as silica. Much more complicated is the nature of the sites that generate positive charges.

The positive sites can be generated by inorganic impurities, such as for example Al_2O_3 . Coal also contains nitrogen [47]: bituminous coals typically 1.5-1.75% and anthracites less than 1%. It is believed that most of the nitrogen in coal is present in ring compounds, predominantly pyridine and quinoline derivatives. These groups, as well as Voll and Boehm's pyrone-like cyclic structures, can also contribute to the creation of a positive surface charge.

The role of oxygen as discussed by Frumkin [19-24], and Garten and Weiss [27], may also be very important in creating positive charge. It is interesting to recall here some electrochemical tests carried out with anthracite in the 60's [48,49]. They included two series of measurements carried out with a freshly prepared anthracite electrode, and with the same electrode exposed to air for a few days under room conditions.

As seen the potential of a freshly prepared unoxidized electrode, measured in aqueous solution versus saturated calomel electrode (Fig. 8), was increasing with time (during the first 30-60 minutes), but decreased abruptly on addition of an electrolyte. This decrease depended on the anion and suggested that the electrode was positively charged.

For the oxidized anthracite electrode the potential was steadily decreasing with time during the first 60-120 minutes, but sharply increased on addition of an electrolyte and this time the increase depended on the valency of the cation

(Al³⁺>Ca²⁺>K⁺). It seems then that while the fresh anthracitic surface was positively charged in water, the same electrode exposed to air for several days acquired negative charge obviously due to its oxidation. These experiments suggest that the same phenomena that occur on carbon black, may also be involved in the creation of electrical potential on surface of coal. Such positive sites on coal surface would then be generated by electrochemical mechanism which may operate only in the presence of oxygen and only if surface is freshly prepared. It is still, however, unclear whether such an electrochemical mechanism may only be involved in setting up the charge on anthracite surface, or also on lower rank coals.

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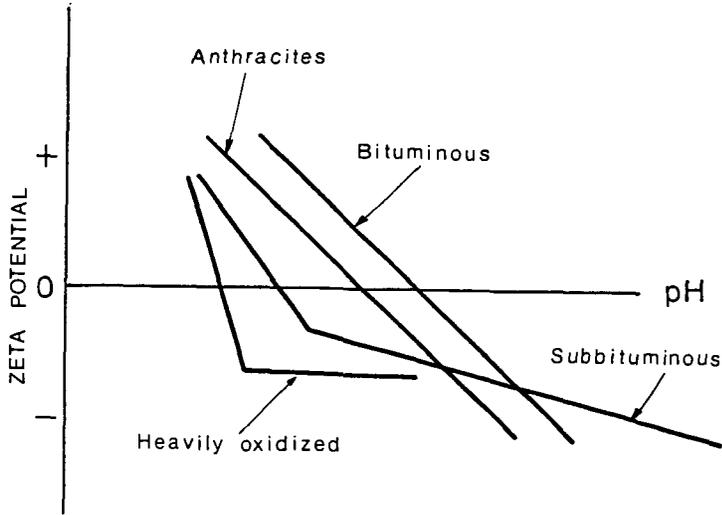


Fig. 1. Schematic microelectrophoretic mobility versus pH curves for different coals [1].

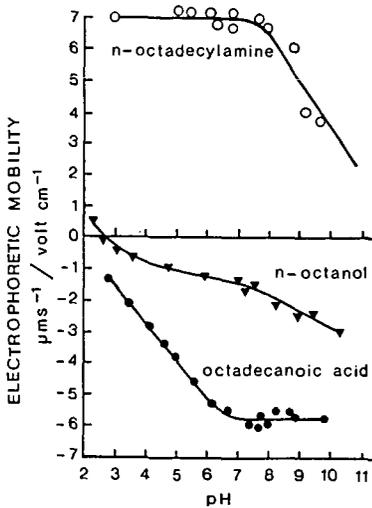


Fig. 2. Electrophoretic mobility against pH relationship for n-octadecylamine, n-octadecanol and n-octadecanoic acid in 0.02 N NaCl [3].

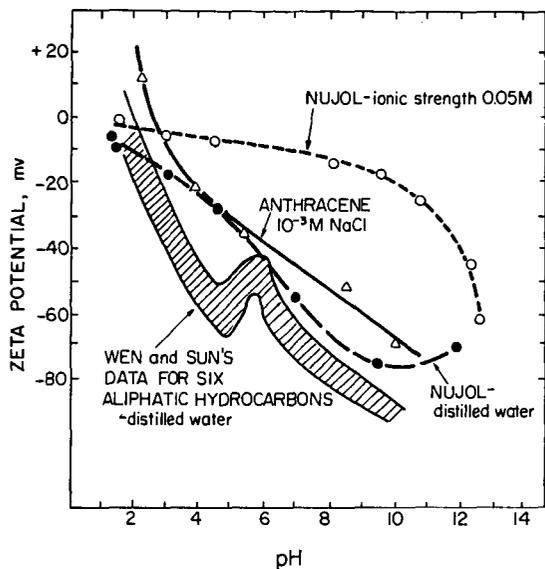


Fig. 3. Zeta potential of Nujol droplets [6], six aliphatic hydrocarbons [7] and anthracene.

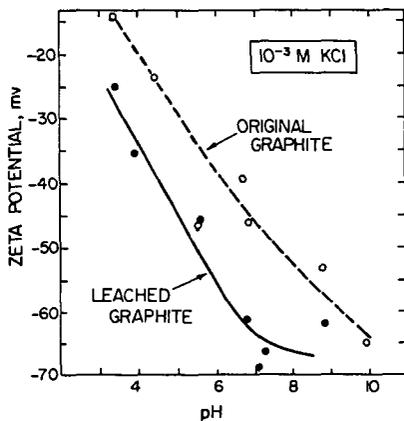


Fig. 4. Zeta potential vs. pH curve for graphite [13].

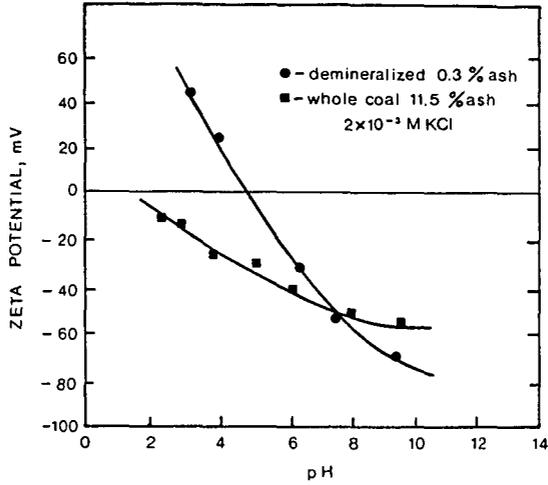


Fig. 5. Zeta potential vs. pH curves for raw and demineralized Somerset mine coal [35].

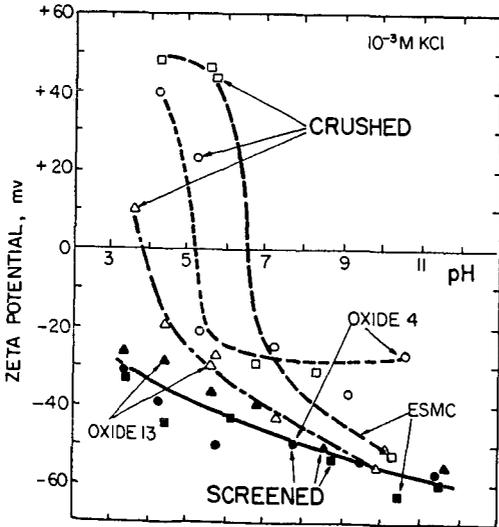


Fig. 6. Zeta potential vs. pH curves for unoxidized metallurgical coal (ESMC), and Fording metallurgical coal: slightly oxidized (Oxide 4) and severely oxidized (Oxide 13) [37].

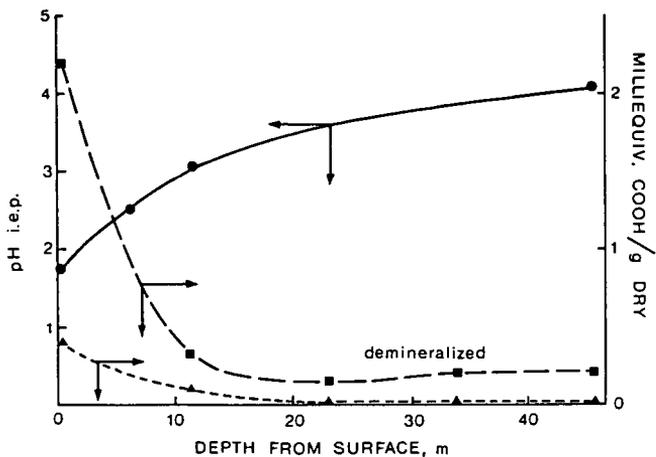


Fig. 7. Iso-electric points and carboxylic group content of coal samples collected from Seam No. 7 of the Fording River Deposit, B.C., at various distances from the surface (adapted after [41,42]).

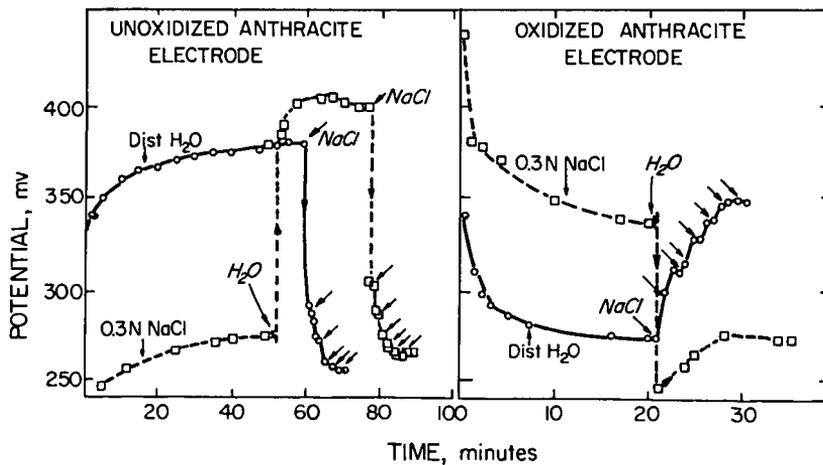


Fig. 8. Potential of fresh and oxidized anthracite electrodes measured versus saturated calomel electrode [48,49].