Effect of Non-ionic Reagent Adsorption on Zeta Potential of Fine Coal Particles

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The -5 μm size fractions of two low rank British coals were used in zeta potential measurements. The electrophoretic behaviour was described by the Helmholtz-Smoluchowski equation. The non-ionic reagents used for the adsorption tests were of diacetone alcohol and 2-ethyl hexanol. Zeta potentials of both coals at various pHs were significantly different in the absence of the non-ionic reagents. Negligible variations were observed on the zeta potential curves of both coal particles in the presence of the non-ionic reagents used. It was concluded that the pH of coal particles in slurry is a principle parameter controlling the value of zeta potentials. As the zeta potential for Bickershaw coal particles was zero at about pH 5, the point of zero zeta potential was not observed for Rawdon coal particles. This is attributed to the functionality and the extent of oxidation of the coal surface.

Key Words: zeta potential, non-ionic reagents, coal

Introduction

The behaviour of coal particles in electrokinetic experiments may provide information on coal surface properties and on the interactions among coal particles suspended in a liquid. Such information may be extremely valuable in explaining both froth flotation of coal, which is based on differences in the surface properties of coal and gangue particles and coal-water properties. Such phenomena depend on the fact that when two phases are in contact a potential difference is developed between them. There are several ways to generate this effect in aqueous systems. The water dipoles may be oriented at the interface, thus creating a potential difference. Ions or excess electrons in one or both phases give rise to a nonuniform distribution of electric charges at the interface between the phases[1]. Surface modification, in particular restoration of hydrophobicity, can be achieved by adsorption of surface active agents or polymers at the coal-liquid interface [2−4].

Studies have been done to describe the role of surface forces in wet cleaning methods of fine coal. These studies have included the need for a maximum hydrophobicity of the coal surface relative to the mineral matter and requirements for the surface charge of the coal[5−7]. It has been suggested that the criterion for hydrophobicity of coal is that it should have a point of zero charge[5,7]. In contrast Jessop and Stretton[8] disagreed with this view. They concluded from their study that a zero point of charge is not a criterion for hydrophobicity and that changes in the electrokinetic potential, ζ, produced by altering conditions, rather than the actual ζ values are important as such changes would indicate whether or not a particular ion or

surface active agent is adsorbed at the surface. Çelik and Somasundaran[9] argue that the contamination of the coal surface as well as oxidation might be responsible for its negative surface charge.

Research has shown that the particle charge of coal was not affected by the adsorption of the non-ionic surfactants such as Triton x-100[3] and polyoxyethylene nonylphenyl ether[10]. Studies were carried out on the adsorption of ionic surfactants[2,3,11,12] on various size fractions of coals. The zeta potentials of coal particles were strongly influenced by adsorption of the cationic surfactant, which was found to be dependent on pH, with the higher solution pH leading to higher surfactant adsorption. Ayub et al. [11] concluded that the adsorption of cationic surfactants involved both electrostatic and hydrophobic interactions with the coal surface.

Çelik[13], and Çelik and Yoon[14] studied the adsorption of ethoxylated sulfonates, non-ionics of the same ethoxylation number and poly (oxyethylene) nonylphenol homologues on a low ash coal. They reported that the adsorption of non-ionic surfactants shifted the zero point of charge of the coal particles from 5 to 7.2 and 6.4. However the particles in the presence of ethoxylated sulfonates exhibited constant zeta potentials. The zero point of charge shift was attributed to the displacement of water molecules by alkyl chain followed by a decrease in dipolar interactions.

A research programme was carried out on the adsorption behaviour of non-ionic reagents on two low rank British coals[15,16] and their influence on the froth structure and flotation performance[16,17]. The aim of this part of the study was to determine the effect of non-ionic reagents (diacetone alcohol and 2-ethyl hexanol) adsorption on the zeta potentials of the -5 μm size fractions of Bickershaw and Rawdon coals.

Theory

Electrical Double Layer and Zeta Potential

In the development of surface charge, whether by ion adsorption from the liquid phase on the particle or ionisation of groups, which exist on the solid surface, the surface acquires a potential with respect to the solution[18]. The potential difference between the surface and bulk solution is termed the total double layer potential, Ψ_0. When a particle moves in the liquid, shear takes place, between the Stern layer (a boundary layer of charge of the opposite sign ions), which moves with the particle and the diffuse layer, the potential at the plane of shear being known as the zeta potential reflects an electrokinetic effect[19]. The total double layer potential Ψ_0, decays exponentially from its value at the surface to zero in the bulk liquid. For a spherical particle of radius $\mathbf{r}$, the potential Ψ at a distance $\mathbf{R}$ from the centre of the particle is

$$\Psi = \Psi_0 \frac{\mathbf{r}}{\mathbf{R}} \exp\left[-\kappa\left(\mathbf{R} - \mathbf{r}\right)\right] \tag{1}$$

where κ is a function of the electrolyte concentration:

$$\kappa = \left(\frac{e^2 \sum \mathbf{n_i^0 z_i^2}}{\varepsilon k \mathbf{T}}\right)^{\frac{1}{2}} \tag{2}$$

$\mathbf{n_i^0}$ is the number of ions of type $\mathbf{i}$ per unit volume having a valency $\mathbf{z_i}$, e is the electron charge, $\mathbf{k}$ is the Boltzmann constant, $\mathbf{T}$ is the absolute temperature and ε is the permittivity of the medium.

The relation between electrophoretic mobility and zeta potential depends on the particle radius and the electrolyte concentration as expressed in the product $\kappa\mathbf{r}$. The term $(\kappa\mathbf{r})$ is a dimensionless quantity,

whereas κ^{-1} has units of length and is often called the thickness of the double layer (or ion atmosphere near a surface) [20].

The $(\kappa \mathbf{r})$ values are considered to determine the method for conversion of electrophoretic mobilities into effective zeta potential, $\mathbf{r}$ is the actual radius of the particle. For $\kappa \mathbf{r} > 200$ Smoluchowski showed that

$$\mathbf{u} = 4\pi \varepsilon_0 \frac{D\zeta}{4\pi \eta} \tag{3}$$

where η is the viscosity of the medium, and $\mathbf{D}$ is the dielectric constant. $\mathbf{D} = \varepsilon / \varepsilon_0$ where ε_0 is the permittivity of a vacuum. This equation is applicable to colloidal dispersions containing high electrolyte concentration.

Experimental

Coals and Reagents

Two low-rank British coals, sampled from the Bickershaw and Rawdon collieries, were chosen for the study. The coals were collected from British Coal. Elemental analyses of the coals used are reported in the Table. The reagents used were diacetone alcohol, DAA, (4-hydroxy-4-methyl-2-pentanon, $C_6H_{12}O_2$), 2-ethyl hexan-1-ol, 2ETH ($C_8H_{18}O$), which are non-ionic.

Table Elemental analyses of the coals used

Element	Rawdon coal, wt%		Bickershaw coal, wt%	
	feed	daf^a	feed	daf^a
C	51.3	78.0	76.0	83.6
H	3.5	5.3	4.9	5.4
N	0.9	1.4	1.5	1.7
O (by diff.)	8.2	12.4	5.9	6.5
S (total)	2.1	3.2	2.6	2.8

^{a}dry ash free

Size Reduction, Particle Size Analysis, Determination of Ash and Moisture Content

The coals were crushed in a cone crusher which produced material of less than 5 mm diameter. The crushed products were then milled in a kek mill for further particle size reduction. The milled samples were sieved by a Locker Rotex triple deck screen. Four size fractions were collected in the collecting vessels: -48 μm, 48-104 μm, 104-250 μm and +250 μm. The -48 μm size fraction of Rawdon and Bickershaw coals were classified into -5μm, 5-20 μm and 20-48 μm size fractions on the air swept classifier at Pennsylvania State University in the USA. The particle size distributions of the -5 μm size fractions of the coals used were determined using a Malvern MasterSizer particle analyser. Figure 1 shows the particle size distributions for the -5 μm nominal size fractions of Bickershaw coal. Particle size parameters for Bickershaw coal d_{10}, d_{50}, d_{90} and d_{sauter}, are also reported in the same figure. There was no significant difference between the particle size distributions of Bickershaw and Rawdon coals. Therefore the figure for Rawdon coal is not illustrated in this article. The particle size parameters of Rawdon coal were 1.23 μm (d_{10}), 4.10 μm (d_{50}), 8.41 μm (d_{90}) and 2.43 μm (d_{Sauter}).

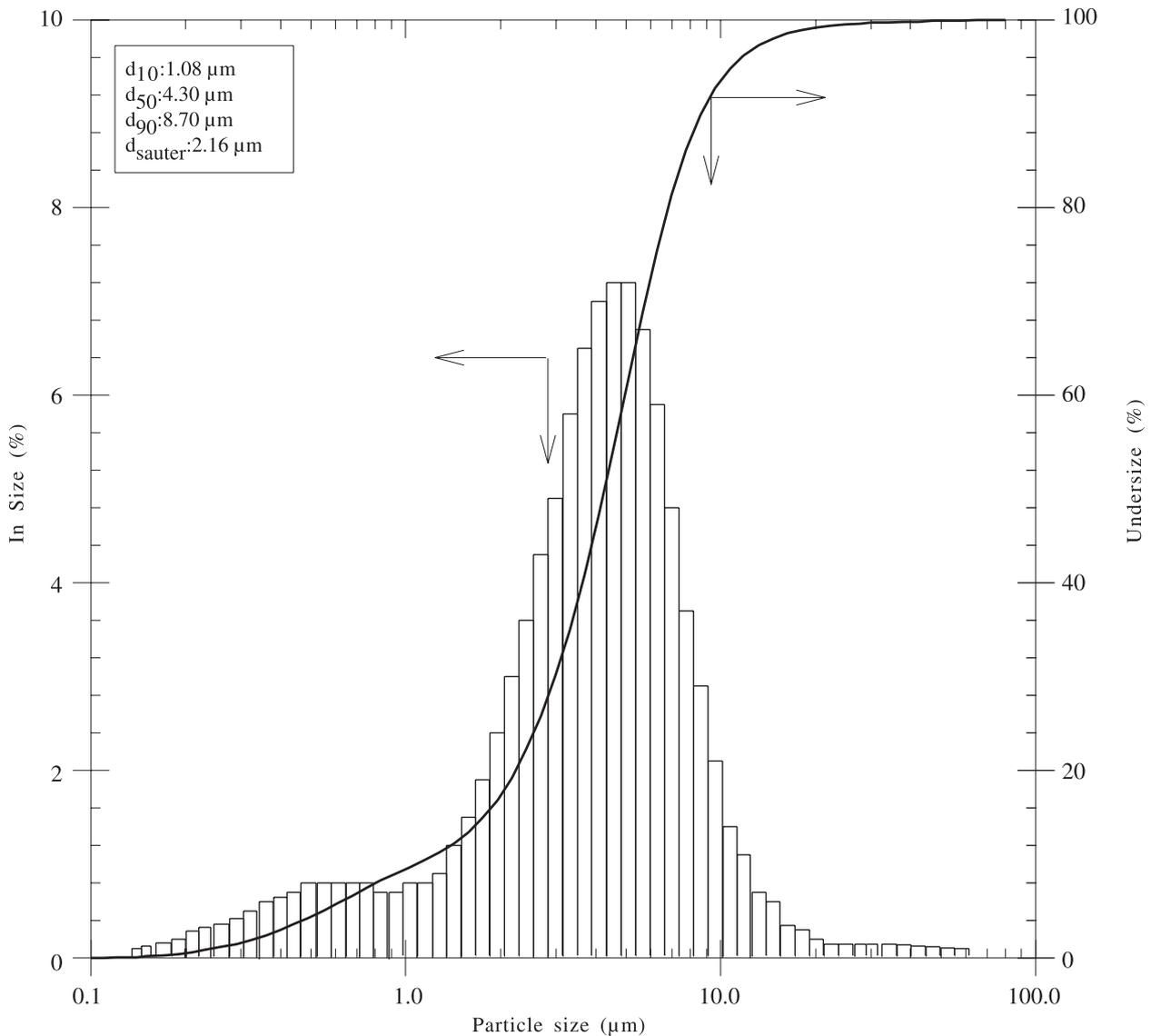**Figure 1.** Particle size distribution of the -5 μm size fraction of Bickershaw coal

The ash contents of the samples were determined according to the British Standard for the analyses of coal and coke (B.S. 1016). The moisture contents of the samples were measured by oven drying over a four hour period. The ash contents of the coals determined were 33.25 % and 8.13 % for Rawdon and Bickershaw coals respectively. The moisture contents of the same samples were 1.1 % and 0.61 %.

Surface areas (BET) of the coal particles were determined using a Carlo Erba Sorptomatic Series 1800 instrument. The tests were performed at the liquid nitrogen boiling point of -195.6 °C. The BET surface areas of Bickershaw and Rawdon coals were 6.65 and 16.78 m^2 g^{-1}, respectively.

Adsorption Tests

The adsorption tests were conducted at room temperature (295 K) in glass vessels with a total volume of 60 ml. Magnetic followers were provided to agitate the slurries by means of a magnetic stirrer. All the

tests were performed under natural pH conditions. The Bickershaw and Rawdon coal slurries were pH 6.8 and 6.6 for the first 10 minutes of the measurements respectively. Blank adsorption tests were performed at room temperature to ascertain whether reagent is adsorbed on the walls, lid and magnetic follower of the adsorption vessel. The adsorption on these parts of the adsorption system was negligible.

Dry coal samples (2.0 grams) were mixed with 20 ml of distilled water in the adsorption vessel for 5 minutes, after which 18 ml of reagent (DAA or 2ETH) solution at the desired concentration was added. Higher initial concentration of 2ETH was added to the slurry as in pure state. The coal solution mixture had a solid content of 5 % and was left to be conditioned for the required time period, 10, 30 and 1440 minutes. A pressure type syringe holder was used to filter the conditioned sample. The filtrates containing DAA or 2ETH were analysed using a Hewlett Packard 5890 Series II Gas Chromatograph.

Zeta Potential Determination

The zeta potentials, ζ (electrokinetic potentials) of the coal particles were obtained by means of a microelectrophoresis technique. The electrophoretic mobilities of the coal particles were determined using a Rank Brothers Mark II Particle Micro-Electrophoresis Apparatus. The measurements were conducted with a slurry of 0.1% concentration using the -5 μm fractions of both coals. All measurements were made in 1×10^{-3} N NaCl solutions. The pHs of the slurries were adjusted using either acid (0.1 N HCl) or base (0.1 N NaOH) solutions containing the same anion or cation as that of the salt.

The electrophoretic mobility measurements were made using the manual timer incorporated in the apparatus. More than twenty measurements were made of fifteen particles each moving in both directions.

Results and Discussion

Reagent Adsorption

The adsorptions of DAA on Bickershaw and Rawdon coals are shown in Figure 2. Contact times for the adsorption tests were 10, 30 and 1440 minutes respectively. Several different initial reagent concentrations (including 5 and 20 mg.reagent/g.coal) were used. The zeta potential measurements of the coal particles were carried out for 10 minutes adsorption. The adsorption isotherms for 30 and 1440 minutes are only given to show whether or not the adsorption process reached the equilibrium level. The initial reagent loadings, 5 and 20 mg/g.coal, were indicated by the arrows on the 10 minutes adsorption isotherms. The amounts of DAA adsorbed on Bickershaw coal surface were 0.250 and 0.689 μM/m^2 for 5 mg/g.coal (2265.5 μM/dm^3) and 20 mg/g.coal (9061.8 μM/dm^3) of the initial reagent loadings, respectively. Surface concentration in the presence of 20 mg/g.coal of the initial reagent loading is 2.75 times higher than that of 5 mg/g.coal of the initial reagent loading. In terms of Rawdon coal, per unit area (m^2) of the coal contained 0.42 and 1.039 μM DAA for the initial reagent loadings; 5 and 20 mg/g.coal respectively. Reagent concentration on the surface is 2.47 times higher in the presence of 20 mg/g.coal of the initial reagent loading compared to 5 mg/g.coal. The results obviously show that the amounts of DAA on the surface of Rawdon coal are higher than those of Bickershaw coal. The adsorption of 2ETH showed different behaviour in terms of the amount of reagent adsorbed. The amounts of 2ETH on Bickershaw coal were 3.707 and 13.40 μM/m^2 corresponding to 5 mg/g.coal (2020.0 μM/dm^3) and 20 mg/g.coal (8080.0 μM/dm^3) of the initial reagent loadings seen in Figure 3. Surface concentration of the reagent increased up to 3.61 times for 20 mg/g.coal of the initial

loading of 2ETH. Figure 3 also shows the adsorption isotherms for Rawdon coal using 2ETH. For 10 minute adsorption time, the amounts of the reagent adsorbed on the coal were found to be 1.799 and 6.30 $\mu M/m^2$ for the initial reagent loadings (that is 5 and 20 mg/g.coal). This shows that the reagent adsorbed on the coal surface is 3.50 times higher when the initial reagent loading is 20 mg/g.coal.
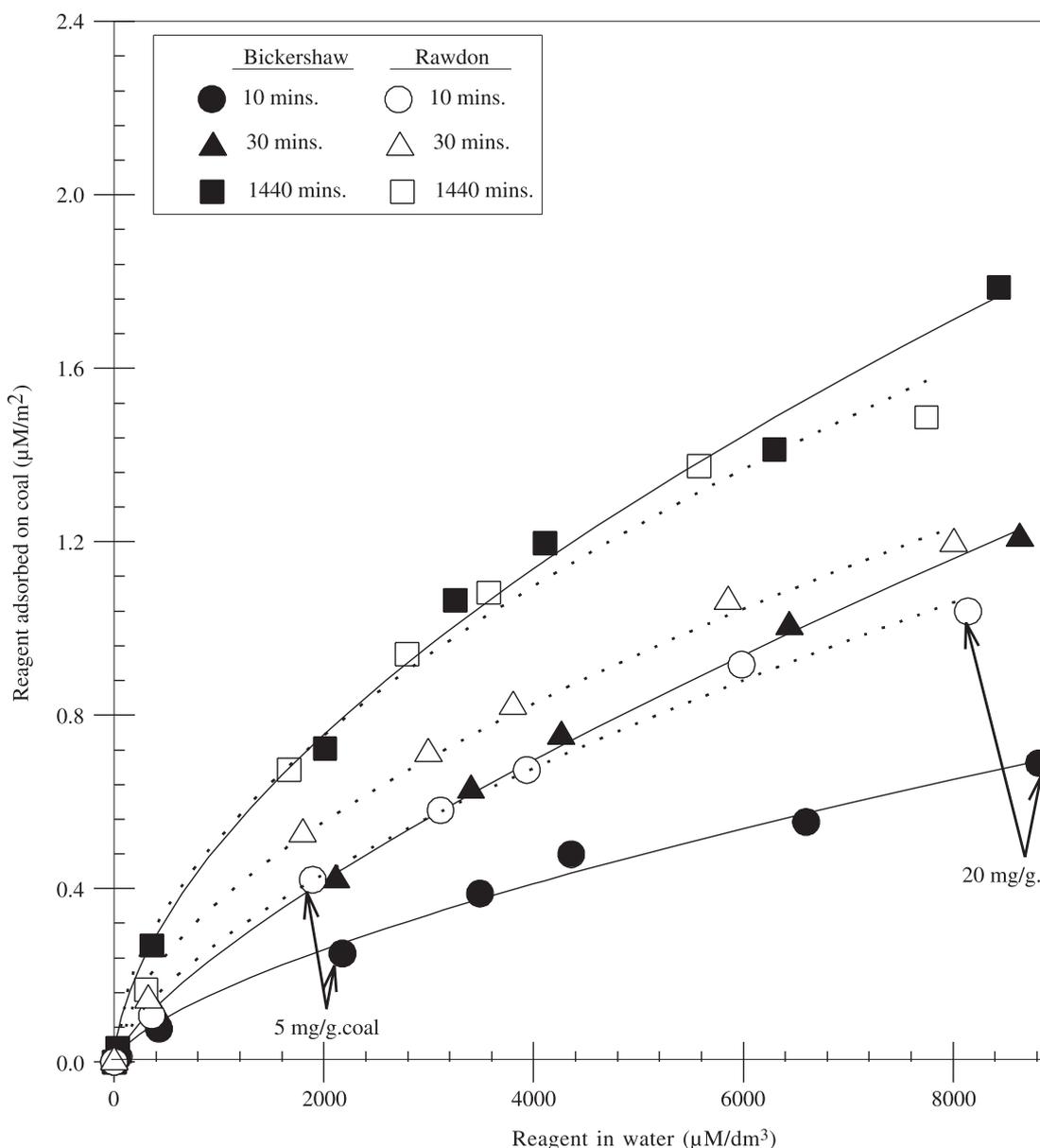

Figure 2. Adsorption isotherms for Bickershaw and Rawdon coals using diacetone alcohol

The specific adsorption of 2ETH per unit area is higher for Bickershaw coal than for Rawdon coal, in sharp contrast to the adsorption of DAA. This reagent (2ETH) has only one functional group in its molecule which is the hydroxyl. However, there are two functional groups, hydroxyl and carbonyl, within the diacetone alcohol molecule. Different adsorption behaviour of the reagents may be attributed to the different surface areas and functionality of the coals, chemical structure and the molecular orientation of the reagents.

Zeta Potentials

Zeta potentials (ζ) of the coal samples were determined using the method reported in the Experimental section. In 0.001 M sodium chloride solution the thickness of the double layer surrounding the coal particles, κ, was 96.18 Å(9.618 nm). The value of the term (κR) was therefore about 259.75, a relatively large value. So the Helmholtz-Smlouchowski equation is valid according to the instruction manual supplied with the microelectrophoresis apparatus. In order to compute zeta potentials from electrophoretic mobilities, this equation was therefore used.

The measurements were conducted with and without reagent for each test. Figures 4-5 and 6-7 show the variation of the zeta potentials of Bickershaw and Rawdon coals with pH at various concentrations of the non-ionic surfactants; DAA and 2ETH respectively. The initial reagent concentrations used were 5 and 20 mg/g.coal for all measurements.
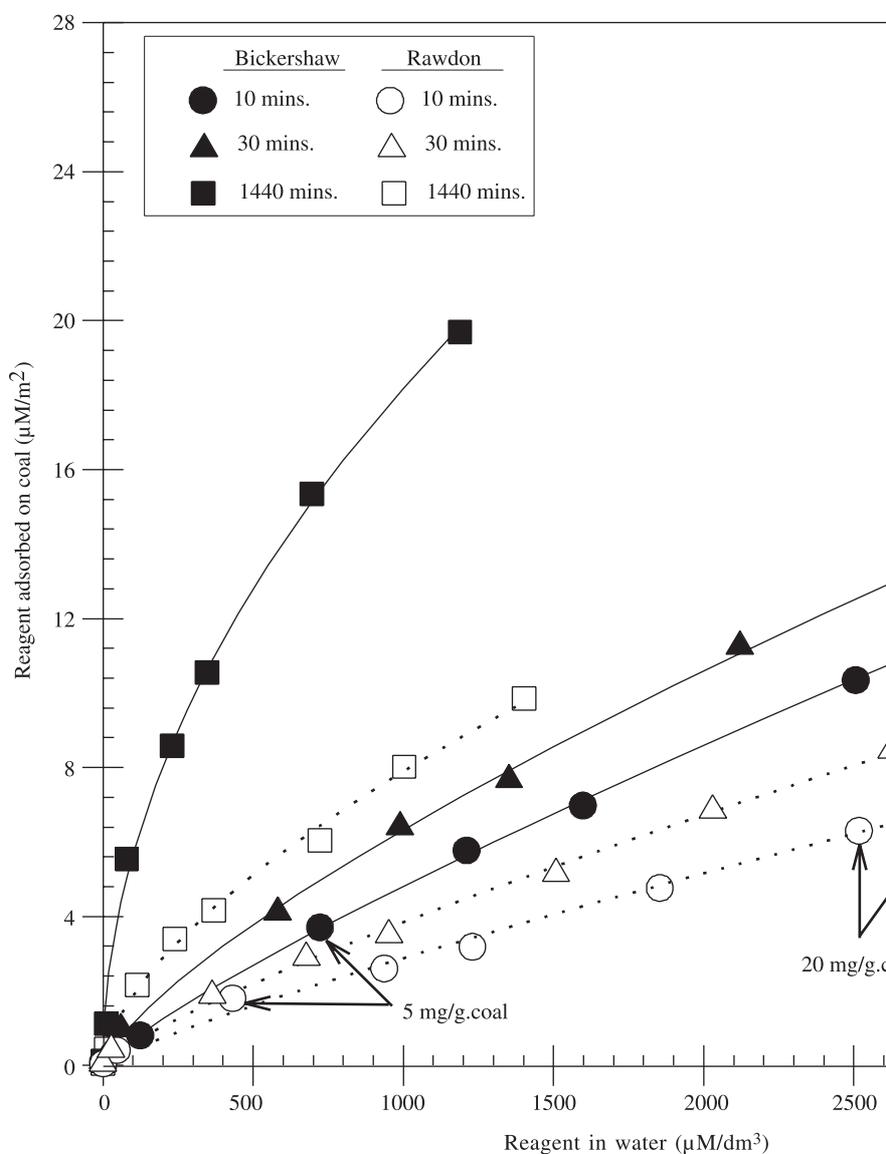

Figure 3. Adsorption isotherms for Bickershaw and Rawdon coals using 2-ethyl hexanol

In the presence of the non-ionic reagents, the zeta potentials of the Bickershaw and Rawdon coal particles did not change significantly. Ayub et al.[3] and Esumi et al.[10] found similar results using non-ionic surfactants for the adsorption tests. For Bickershaw coal, over the pH range 3.5-6.0 the zeta potential lies in the range of +20 mV to -20 mV. The point of zero charge for Bickershaw coal occurs at a pH of 5.

The results obtained from previous studies[16,17] showed that the flotation performance of the -5 μm size fraction of Bickershaw coal was perfect in the presence of both DAA and 2ETH.
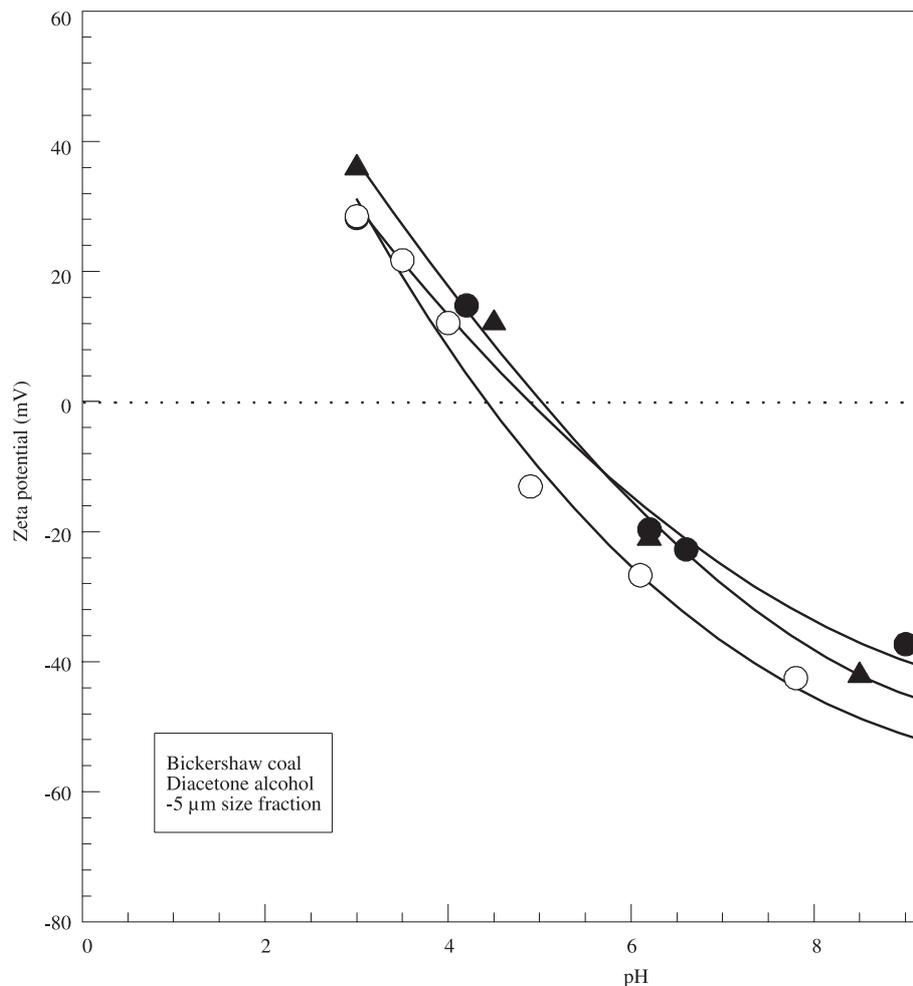

Figure 4. The variation of the zeta potential for Bickershaw coal with change in pH using diacetone alcohol

In Figures 6 and 7, the zeta potentials were negative over the whole pH range for Rawdon coal in the absence of the reagent. When DAA or 2ETH is used at different initial loadings, no significant differences were observed at the zeta potential values.

The flotation tests for Rawdon coal[16,17] were also carried out in the presence of 2ETH and DAA. Interestingly, while the coal floated in the presence of 2ETH, the use of DAA did not work with the coal as a flotation agent.

The adsorption tests (Figures 2 and 3) showed that 2ETH was adsorbed at least 5 and 15 times more than DAA on the surfaces of Rawdon and Bickershaw coals, respectively. These amounts of 2ETH on the coal particles did not significantly change the zeta potentials of either, coal. Since the ionic strength of the slurry solution was the same for all the tests, then it can be considered that the thickness of the electric

double layer may not be affected by adsorption of the non-ionic reagents used in this study. On the contrary, as reported in available literature[3,4,10−12], the ionic (anionic or cationic) reagents change the zeta potential of the solid particles noticeably.

Functionality of the coal surface also plays a very important role, the electrokinetic behaviour of the coal particles. Probably, the functionality of Rawdon coal is fairly different from that of Bickershaw coal. Not enough is available regarding functional groups present on the surfaces of the coals used in this study. However, the oxygen contents of the coals are given the Table. As is well known, the properties of the coals are strongly dependent on the oxygen content. This is clearly consistent with Rawdon coal results indicating the negative charge on the coal surface to be derived from the phenolic hydroxyl and carboxylic groups. The state of surface oxidation of the coal properties should also be considered in determing the zeta potentials of the particles in the slurry.

The ion concentration increases by dissociation of ionogenic groups or decreases by re-adsorption of some ions in solution on the solid particle surface. As a result of this, the thickness of the electrical double layer around the particle becomes thinner or thicker, thus electrophoretic mobility of the solid particle changes. In the case of Rawdon coal, the electrolyte concentration may have been changed due to high mineral content and dissociation of ionogenic groups on the coal surface.
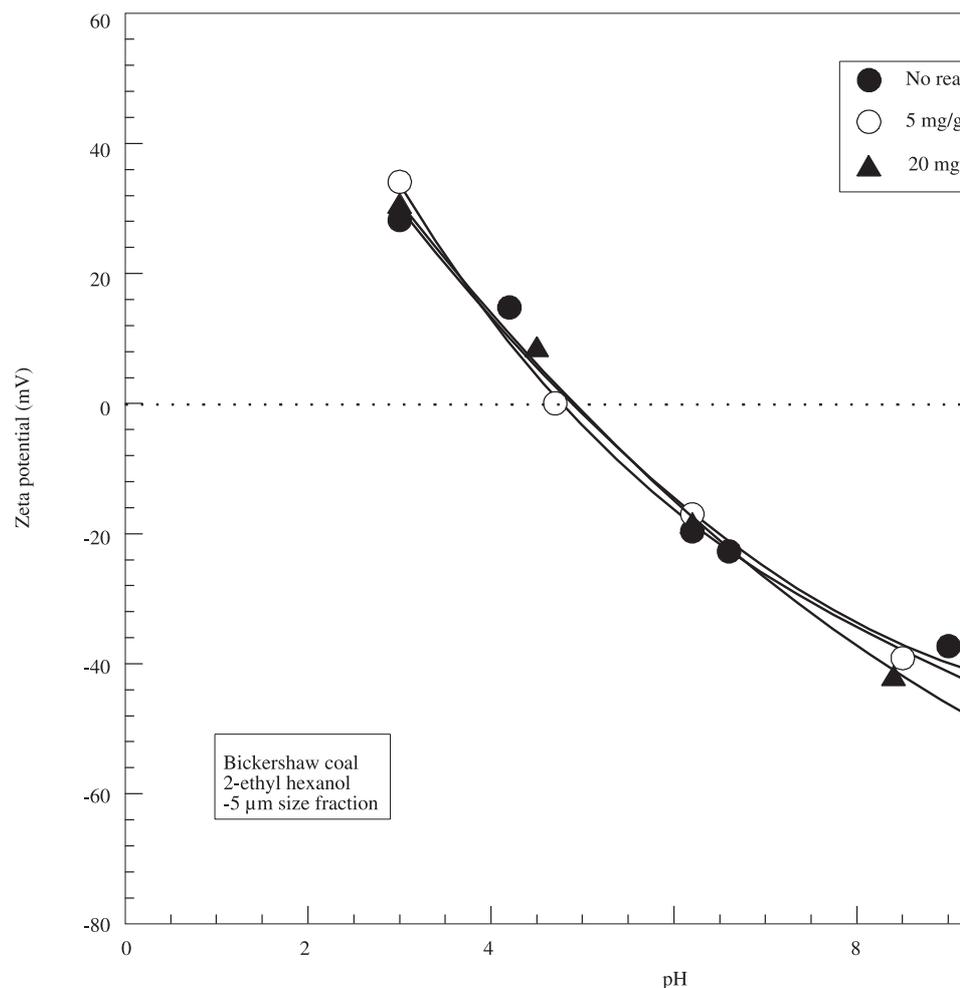

Figure 5. The variation of the zeta potential for Bickershaw coal with change in pH using 2-ethyl hexanol

It is obvious that the charge distribution of the solid surface should be considered Because pure coal particles (completely liberated) and particles with minerals (partially liberated) may behave significantly different during the electrokinetic measurements. In short liberation of the coal particles in addition to the functionality of the coal surface and electrolyte concentration may be important for dermining the electrokinetic properties of the coal particles.
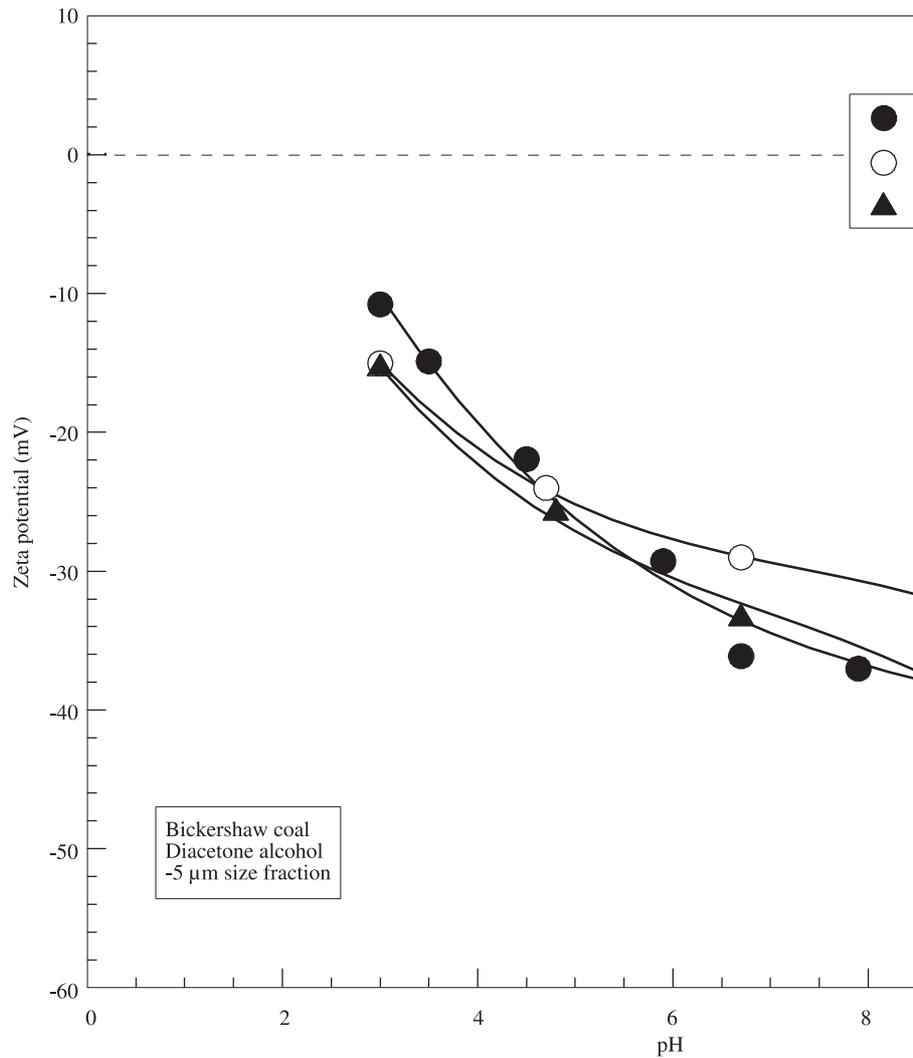

Figure 6. The variation of the zeta potential for Rawdon coal with change in pH using diacetone alcohol

Negative zeta potentials were obtained in acidic and basic media for Rawdon coal particles (Figures 6 and 7). Bickershaw coal (Figures 4 and 5) showed both negative and positive zeta potentials in the range of pHs between 3 and 11. While negative zeta potential varied in a broad pH range (5-11), positive zeta potentials were observed only in rather acidic media (3-5). Very small variations on the zeta potential curves of both coal particles shown in Figures 4-7 may be due to experimental errors and do not appear to be significant.

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Conclusions

1. The increase of the concentration of non-ionic reagents, DAA and 2ETH, on the surfaces of the coals had no effect on the observed zeta potentials.

2. It was found that the pH of coal particles in slurry is a principle parameter controlling the value of zeta potentials. As the zeta potential for Bickershaw coal particles was zero at about pH 5, the point of zero zeta potential was not observed for Rawdon coal particles. Also the coal particles in the presence of the reagents, both DAA and 2ETH, did not show the point of zero zeta potentials. This is attributed to the functionality and the extent of oxidation of the coal surface. Therefore the magnitude of the zeta potentials of the particles in the slurry is greatly dependent on these factors.

3. The electrophoretic behaviour was described by the Helmholtz-Smoluchowski equation. The thickness of the diffuse double layer (κ) computed was 96.18 Å.
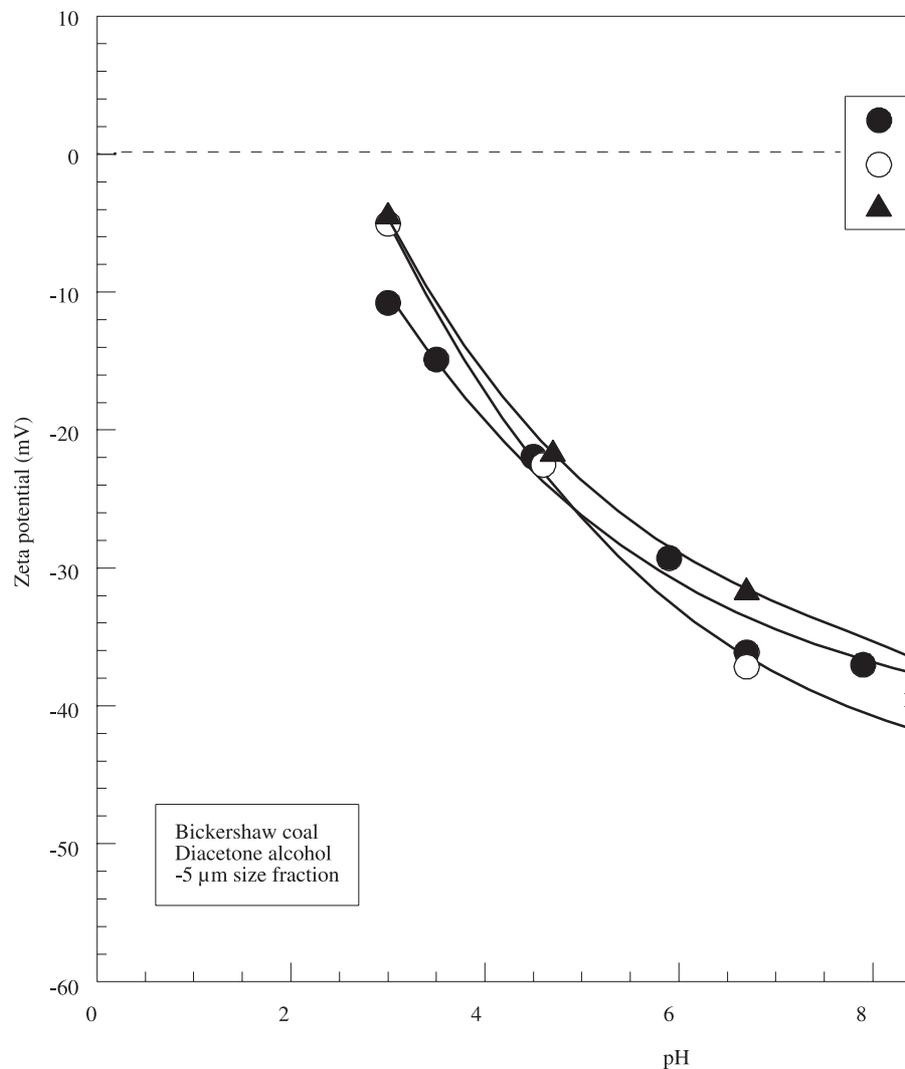

Figure 7. The variation of the zeta potential for Rawdon coal with change in pH using 2-ethyl hexanol

Nomenclature

D	:	Dielectric constant (dimensionless)
R	:	Distance from the centre of the particle
T	:	Absolute temperature
V	:	Volt
d_{10}	:	Particle size diameter at percentage point, 10%
d_{50}	:	Particle size diameter at percentage point, 50%
d_{90}	:	Particle size diameter at percentage point, 90%
d_{Sauter}	:	Sauter Mean Diameter
e	:	Electron charge
k	:	Boltzmann constant
mV	:	Millivolt
n_i^o	:	Number of ions of type **i** per unit volume having a valency $\mathbf{z}_i$
r	:	Radius (spherical particle)
u	:	Particle mobilities
z_i	:	Valency (ion)
ε	:	Permittivity of the medium
ε_0	:	Permittivity of a vacuum
η	:	Viscosity of the medium
κ^{-1}	:	Thickness of double layer (or ion atmosphere near a surface)
μM	:	Micromoles/dm^3
μm	:	Micrometer
Ψ_0	:	Total double layer potential
Ψ	:	Potential at a distance R from the centre of the particle
ζ	:	Zeta potential of the coal particles

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