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Surface Properties of Fine Coal Particles in Aqueous Surfactant Solutions. Adsorption and Electrokinetics.

by

C Abdul Latiff Ayub

A Thesis

submitted in partial fulfilment of the

🦯 requirements for the degree of 🕚

Doctor of Philosophy

at Dalhousie University

August, 1984

For

Shanta Kumarie'

,who suffered and survived through it all

			• "'' ``
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ABSTRACT

with an ever increasing world demand for energy, and the escalating costs of oil and gas, coal is increasingly seen as the primary future energy resource of many nations. However, combustion of coal, our most abundant fossil fuel, can create serious environmental problems. Goal as mined contains significant amounts of impurities including sulfur bearing minerals. In addition, to satisfy future needs we will have to switch to coals containing even higher amounts of ask and sulfur, because the supply of high quality coal will have been exhausted. Thus, we may foresee an ever more important role of coal cleaning processes before utilization in combustion or conversion processes. There will be a need to go to very fine grinding of run of the mine coal to improve mineral liberation. Evidently, this will also lead to more complicated fines separation processes. Many coal beneficiation processes such as flotation, agglomeration, selective flocculation, etc. exploit the difference in surface properties of the coal and its attendant impurities and hence studies of the surface properties of coal will become more and more important. In recent years, considerable attention has been devoted to the use of electrokinetic methods to determine the modification of the coal-water interface caused by adsorption of surface active agents.

This thesis describes a systematic study of the properties of the coal-water interface for a high volatile bituminous Eastern Canadian coal in the presence of salt, some simple organic molecules, a nonionic surfactant and several cationic surfactants. The coal fines are from the Cape Breton Development. Corporation, Nova Scotia, Canada, Victoria Junction washing plant. The interfacial properties have been studied by means of direct adsorption measurements and electrokinetic methods, i.e. microelectrophoresis and streaming potential measurements. As a result of this work, a new method for the measurement of free cationic surfactant at low concentrations in 'coal suspensions has been developed.

Cationic surfactant adsorption on coal increases with hydromobic chainlength as well as with increasing suspension pH. From adsorption isotherms obtained, surface areas and free energies of adsorption were determined. Electrokinetic studies show that surfactant adsorption on coal may depend on particle size under certain local fonditions.

From the combined adsorption and electrokinetic results, a mechanism which involves both electrostatic- and hydrophobic bonding has been proposed for the adsorption of cationic surfactant on coal surfaces.

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•	LIST OF PRINCIPAL SYMBOLS USED
With	reference to the equation or chapter where introduced
ŧ	
, a ,	activity of component i (TIL.3):
	= concentration of component i
, C -	concentration; $c_{1,0} = concentration of component i$
, <i>•</i>	, at point where $\psi = 0$ (11.2)
ę	charge of proton (11,2);
E	streaming potential (II.18);
' G 🔩	Gibbs free energy (II.13);
I,	ionic strength (II.7); current flow (II.30);
k	Boltzmann constant (II.2); partition coefficient
۲L ۳	(111.4);
ĸ	equilibrium constant (II.10);
Kpot*	potentiometric selectivity coefficient (III.4);
, L	Avogadro's number (II.12);
n	number of moles; ni = number of moles of component i
•.	(II.8); chainlength (V.2);
, P	pressure (II.18);
Q	electric charge (II.20);
r ,	radius of ion (V.1);
R.	gas con s tant (II.26);
S	entropy (II.26);
t.	
τ Ψ	absolute temperature (II.2):
+	

u	mobility; u _e = electrophoretic mobility (II.16); u
e/ - V	= mobility of component i (III.4);
V.	velocity (II.14);
V y	volume (II.9);
x	number of moles adsorbed (II.10); $x_m = number of$
•	moles adsorbed at monolayer (II.10);
x	electric field (II.4);
Ž	valence of ions (II.2);
ł	
*	GREEK
•	° • • • • • • • • • • • • • • • • • • •
r	adsorption density of ions (V.3);
∙€ ,	dielectric constant (IF.I);
ζ,	electrokinetic potential;
้ท	viscosity (II.14);
¢* .	interaction of each CH ₂ group of adjacent surfactar
,	ions (V.3);
. [¢] нс	interaction of surfactant headgroup with surfac
₹	(V.3);
ĸ	Debye-Huckel parameter (II.1); specific conductivit
54 2 2	of bulk solution (II.18); $\kappa_p = \text{specific conductivit}$
•	of liquid in the porous plug (Vil); $\kappa_s = surface$
•	conductance (VI.1);
ρ	<pre>space charge density (II.1);</pre>
σ 🖕	area of a site on a solid (II.12);
Σ	specific area of solid (II.12);
	· , · · · ·
•	, •

Volta potential (II.1); ψ_0 = surface potential (II.5); ψ_{δ} = electric potential at outer Stern plane.

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4.0

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CHAPTER[°] I

GENERAL BACKGROUND

I.l <u>Introduction</u>

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History documents the key gole of energy and the problems of fuel scarcity. For instance, in ancient Babylon, deposits of bitumen were discovered and quickly used to provide fuel for the smelting of metals and the heating of buildings. When the bitumen deposits were exhausted, the Babylonian civilization disappeared (1). The rise of Crete as a producer and exporter of bronze weaponry was based on the use of forest fuels (2). That society's decline resulted from deforestation. The salvation of Great . Britain's iron industry, when faced with similar deforestation, resulted from the successful substitution of coal-based coke for wood-based charcoal (3). In Babylon and Crete, for want of energy a civilization was lost. In England, a new source of energy was found and used widely. With the oil embargo in 1973, the North American political structure became aware that oil and gas resources are finite and would not suffice to fuel their economies. This has led to the current attempts to develop a rational, ' long-term energy policy. Conservative estimates (4) of energy resources show that by the year 2000, 20 percent of the energy used in North America will come from oil and

gas, 15 percent from nuclear sources, 5 percent from solar energy and about 5 percent from other sources (hydro, geothermal, etc.). Therefore fifty-five percent must come from other sources, presumably fossil fuels. Since coal constitutes more than eighty percent of North American fossil fuels which can be used with improved technology, a natural result of governmental attention has been the flow of money into chemical research of coal. As a result, coal, which for several decades played a steadily diminishing role in the energy economies of industrialized nations; has once more moved onto the center stage of the energy scene.

Although it is known where most of the coal in Canada is and how to mine it, there is a growing realization that, despite what is understood about coal mining, it is necessary to learn more if coal is to be taken out of the ground and used in a way that is acceptable to society at. large. It is well known that with the focus on acid rain caused by SO_2 and NO_x emissions from fossil fuel combustion facilities, perhaps the major constraining factor to increased coal-utilization, especially in regions where the coal is high in sulfur, is atmospheric emissions. Of longer ' term but no less important concern is the issue of global warming caused by the "Greenhouse Effect". In turning from conventional oil as its major'source of energy to coal and uranium às its most abundant fuels, the world may become trapped in an environmental vice between, radioactive nuclear waste and CO2, SO2, NOx effects from combusting .

fossil fuels, at least if research and development does not come to the rescue. Hence, development of efficient coalcleaning methods such as selective flotation and other processes dependent on interfacial properties e.g. flocculation and spherical agglomeration, designed to upgrade run of the mine coal, is vital in view of the current energy development requirements. Furthermore, coalcleaning processes are mandatory if coal is to be an environmentally acceptable fuel. It is for these peasons that a study of an Eastern Canadian fine coal was undertaken.

I.2 Chemical structure of coal ...

Complete elucidation of the structure of coal has remained beyond the capabilities of the organic chemist and his instruments. However, increased attention has begun to give results and although good structural models for coals and a reasonable understanding of their chemistry still seem like a distant goal, the quantity and quality of work being done now is such that answers to some of the fundamental questions will be found in time to be of some aid to the development of conversion and cleaning processes.

It is generally known that coal is a complex, heterogeneous mixture of high molecular weight substances. Aromatic ring systems and condensed aromatic ring systems are present and these condensed nuclei increase in size and

form an increasingly greater part of total substance as the rank of the coal increases. Whitehurst (5) reported that the aromatic content increases from about 40-50 percent for sub-bituminous coal to over 90 percent for anthracite. Aliphatic structures exist as methyl groups and possibly as side chains containing two or more carbon atoms, as connecting chains between aromatic nuclei (6). Oxygen, present in low and intermediate rank coals, occurs predominantly as phenolic or etheric groups with lesser amounts of carboxylic acids or esters; some carbonyls have also been identified (7). However, these types of structures practically vanish as the coal attains about 90 percent carbon content. It is generally agreed that the nitrogen present has come from plant and animal proteins, from nitrogen-rich bacteria and from plant alkaloids and that it is present in coal as pyridine or pyrrolic type, rings. Sulfur is found/as inorganic and organic sulfur. Inorganic sulfur is found mostly in pyrite but some is found in sulfate. Organic sulfur is thought to occur in thiols, sulfides and thiophenes (8). A number of workers has attempted to develop a representative structure of coal which is consistent in its oberved chemistry (9,10). A recent model is shown in Figure I.1 (10). The structure is consistent with the highly substituted aromatics and with the functionalities which are known to be present in coal. The arrows indicate a number of relatively weak bonds which can account for the rapid breakup of coal into

'Figure I.l Representation of functional groups in coal. (10)



smaller more soluble fragments.

Finally, one of the discernible structural features of coal is the pores within the organic matrix, which are of varying sizes and shapes of $10^{-9} - 10^{-5}$ m in diameter. The porosity of coal is perhaps due to the poor alignment of the main building blocks of coal i.e. the aromatic and hydroaromatic units (11). Minerals and organic debris can often be found lodged within the pores. The standard classification of pores of different sizes is as follows . (12): pores > 50 nm in diameter are macropores, pores 'with diameters in the range 2 - 50 nm are mesopores, pores with diameters in the range 0.8 - 2 nm are micropores and pores < 0.8 nm in diameter are submicropores. Porosity of coal has a great influence on its surface properties and on its behavior during mining, coal-preparation, utilization and transport of coal slurries. Although coal is visibly heterogeneous in composition, there are many regular and repeating features which have definable physical or chemical structures. A thorough knowledge of these features is indispensable for understanding the behavior of coal in various physical and chemical processes such as conversion to liquid and gaseous fuels, benefication, combustion and weathering.

I.3 Classification of Coal

Since coal is a heterogeneous substance usually containing mineral matter and water as impurities,

classification is a matter of some difficulty. Most systems (13,14,15,16,) are based upon some characteristic property of the coal series that changes uniformly and progressively with increase in rank as the series is ascended. The properties generally used for this purpose are either Ultimate Analysis or Proximate Analysis. A coal's position in the continuous series ranging from

peat -> lignite -> sub-bituminous -> bituminous -> anthracite

determines its rank. As shown in Table I.1, the rank of a coal is characterized by its fixed carbon, volatile matter and calorific value (17, 18, 19). In Great Britain, Europe and the U.S.S.R., classification is somewhat different. The National Coal Board of GreatBritain classification is perhaps the most comprehensive in use to day. This is based on the percentage volatile matter at 1200K on a dry, ashfree (daf) basis and the character of the residue obtained by carbonizing coal at 900K in a Gray-King test (20). Table I.2 shows the elemental composition of various Russian coals and the respective nomenclature (21,22).

The different bands of coal which constitute a coal seam are the coal types (16,23). The macroscopically recognizable coal types are termed the lithotypes. Lithotypes are of four kinds (23):

(a) vitrain: a narrow, brilliantly black, glossy or vitreous band which fractures conchoidally, or in small cubes and appears structureless to the unaided eye.

		Table	1.1	د 4
o Û	Classification	of coal	by rank (16,	17, 18)
Class	and Group Fixed (d	l Carbon mmf) ३	Volatile Mat (dmmf) %	ter Calorific ¹ Value (Btu/1b)
I. And 1. 2.	thracite Meta-anthracite Anthracite	>98 92-98	<2 2-8	
3. II. B: 1. 2.	Semi-anthracite ituminous Low volatile Medium volatile	78-86 69-78	8-14 14-22 22-31	 **
3. 4. 5.	High volatile A High volatile B High volatile C	<69 [,] 	>31	>14,000 13,000-14,000 10,500-13,000
111. š 1. 2. 3.	Subbituminous Subbituminous B Subbituminous C		,	10,500-11,500 9,500-10,500 8,300- 9,500
IV. L: 1. 2.	ignite Lignite A Lignite B °		8 e 4 n	6,300- 8,300 <6,300

¹Coals having 69% or more fixed carbon on the dry mineralmatter-free basis (dmmf) shall be classified according to fixed carbon regardless of calorific value

F

* .

4 1.

L

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Twpe ,	Ach	Volatile	Chemi	ral Anal	vel is)
	, · · /	Matter	C	H	S	(N + 0)
D	1-3	39-40 ູ	79-80	5-6	, <u>1</u>	11-15
G	- 2-3	30-44	78-86	5 6	2	9-14
Zh	ُ 3 _,	30	90	5	l,	[•] 5
K `	3	21-22	88 -91	4-5	1	2-3
Т.	2-3	9 - 16	92-94	4	1-2	3-4
A	3	8	95	ົ2	-	3
¢	n				*	- *
					• •	L
4		• ** *			, -	*
8 1		e, N		د بر		
- -					'n	, t
		5 K				¥
n	,	¢	a A	•	÷	
	σ			.	"	υ
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	,	Ð			ι	ı
, u			-			

(b) clarain: a black, often horizontally striated, layer or lenticular mass which has a silky lustre and which presents a glossy surface when freshly broken.

(c) durain: a dull grey-black material which possesses a tight granular structure and which breaks to display fine-grained or mat surfaces.

(d) fusain: , a soft coal which breaks readily into , fibrous strands or to a powder and occurs , chielly as patches or wedges.

Although, this terminology is fairly generally used for indicating the various rock types, this purely macroscopic differentiation is now considered inadequate. The true petrography of coal starts with the microscopic. examination.

Lithotypes are themselves complex aggregates of more or less homogeneous microscopic constituents called macerals (17). Macerals present themselves in three main maceral groups and the groups, in turn, occur in a variety of associations termed microlithotype groups. In contradistinction to the lithotypes which have the suffix "-ain", the macerals have name termination "-inite" while the microlithotypes have the suffix "-ite". A study of the macerals has shown that the fraction of the total carbon in aromatic structures increases in the order

exinite < vitrinite < inertinite</pre>

while the hydroxil content decreases in the same order (24). However, hydrophobicing of the lithotypes usually increases in the order (25)

fusain < durain < clarain < yitrain

٣

Table I.3 lists some individual macerals and maceral groups now recognized by the International Committee for Coal Petrology (ICCP) (16,17). As the coal is oxidized, its hydrophibicity decreases. In oxidized coal, the amount of hydroxyl and carbonyl groups increases as compared with the natural coal.

^{*} I.4 Impurities associated with fine coal

Most coal conversion processes have specific limits as to the amount and/or composition of impurities of coal, in order for that coal either to be acceptable for the process or to optimize the conversion process itself, e.g.coke production, combustion, coal liquefaction. A detailed knowledge of coal mineral matter is therefore imperative for proper evaluation and maximum use of coal reserves.

Two types of mineral matter are usually encountered in run of mine coal: (a) impurities inherent in the coal seam incurred during deposition and (b) shales, clays and rocks which immediately adjoin the coal seam and are unavoidably extracted with it. Brown (24) lists the important constituents as quartzite, calcite, kaolinite, micas, feldspar minerals, pyrite, marcasite and gypsum. Sulfur may occur as sulfate, as organic sulfur, and in pyrite. The sulfate content is usually low ($\simeq 0.02$ %). The organic sulfur is part of the molecular structure of the coal. Basically, only pyritic sulfur may be partly removed by flotation or other physical separation methods provided the pyrite particles are not too small to be liberated. Gypsum

Table I.3

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Classification of coal (16,17) `

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;,

Megascopic	•	Microscopic	۰ .
Lithotypes	Group Macerals	Macerals	Microlithotype Group
	an a fair an		an albert aller fillen Albert Berneriker Blein Berneriker (han berneriker Berneriker) 19
yitrain	vitrinite	collinite, tellinite	vitrite
Clarain	vitrinite dominant	collinite, tellinite	
-	exinite	sporinite, cutinite, waxes and	•
•	<i>·</i> ,	resins	clarite
·	inertinite less prominent	fusinite, micronite, scleronite	and
	•	semifusinit	e durite
Durain	inertinite dominant	fusinite, micronite, scleronite semifusinit	and ce durite
	vitrinite	collinité, tellinite	a
	exinite less prominent	sponnite,	
	•	waxes and resins	clarite
Fusain	inertinite	fusinite	fusite

may be depressed by lim if it has a tendency to float (26). Table I.4 shows some typical minerals found in coal (27).

1.5 Problems of fine coal preparation

Four priority areas for research in coal preparation are lithotype separation, fine coal cleaning, pyrite removal and pollution abatement. With the depletion of high-grade ore deposits in the future and the increased mechanization of mining methods, producing large amounts of fines that are difficult to clean by conventional methods such as gravity concentration, new methods or improvements of existing methods of coal benefication must be developed. It is probably convenient to consider each of the four basic problems of coal preparation in order to demonstrate the possible application of surface dependent processes and to illustrate the need for a fundamental understanding of the surface characteristics of coal.

Maclean (28) suggests that flotation was the logical process for recovering -48 mesh coal, yet its adoption has been slow. The reasons, as suggested by Mitchell (29) are (1) marketing problems with fines (2) cost of dewatering (3) indifferent test results in removing sulfur (4) inability to make clean separations with the finer sizes and (5) the inability to clean slurries containing a high percentage of clay. However, recently, there has been a rapid growth because (1) flotation has proved an excellent

Table	I.4	۴ ۹
-------	-----	-----

Minerals found in coal (27)

Group	Minerals
Shale	illite,montmorillonite, muscovite
Kaolin	kaolinite, levisite, metahalloysite
Sulfide	pyrite, marcasite
Carbonate	calcite, siderite, dolomite
Chloride	halite, sylvite
Accessory minerals	quartz,gypsum, chloride, rutile, hematite, sphalerite, magnetite, feldspar.
· ε - 1	· · · · · · · · · · · · · · · · · · ·
, " , "	، • • • • • • • • • • • • • • • • • • •
· · · · · · · · · · · · · · · · · · ·	
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means for mitigating the preparation plant "black water" problem, and with substantial increases in the value of coal and its costs of production, the fines previously wasted have become a very valuable product. The lithotypes of coal have different properties (30). These differences are reflected in their effects on coal technological processes such as carbonization, gasification, hydrogenation. If the lithotypes could be readily separated, the products could be sold as individual commodities or as blended products/to meet various requirements of coking or other chemical and thermal processes. The separation and degree of blending would depend upon the particular end use. Specific products would be made for particular applications. The surface characterists of individual coal lithotypes are virtually unknown.

As mentioned in Section I.4, sulfur exists as (1) pyritic (2) organic and (3) sulfate sulfur. The organic sulfur cannot be directly removed by coal preparation procedures. It can only be removed if the entity in which it occurs is removed. On the other hand, sulfate sulfur is easily removed in most preparation practices. Pyritic sulfur in coal is very difficult to remove. One approach suggested for pyritic sulfur removal is liberation by fine grinding and then flotation (28,31). Again, because of limits on air and water pollution, the use of coal as a fuel will be affected directly because of acid mine drainage and black water discharges from preparation plants and because of the sulfur content in stack gas discharges from power plants, the number one consumer of coal.

An understanding of the surface properties of coal as they affect processes like flotation, flocculation and agglomeration would be an important beginning towards the realization of a solution to these problems. Perhaps a study of the adsorption of surface active agents and how they affect the electrokinetic properties of coal surfaces would elucidate the mechanisms associated with coal flotation, establish the existence of any interactions and delineate, to a great extent, the behavior of various froth flotation reagents.

I.6 Coal beneficiation reagents

The previous sections mentioned the various problems associated with the utilization of fine coal as an energy resource and suggested some methods of coal beneficiation. These separation processes, which include flotaten, agglomeration, aggregative flotation and selective flocculation, depend on the alteration of the surface properties of fine coals in water through the action of various surface active agents. Furthermore, there has been recent interest in employing multi-stage flotation processes to deep-clean coal to less than 1 or 2 percent ash so it can be used as an ideal feedstock for coal-water mixtures.

There are several challenging surface chemical

problems associated with these new developments. The problem of selectively recovering fine particles by flotation has long been recognized but not resolved. It is generally assumed that the properties of coal surfaces such as wettability, air-water contact angle and electrokinetic potential are dependent on the adsorption of surface active molecules at the coal-water interface. For example, dewatering of coal, which is an indispensable step in the production of upgraded clean coal, is favored by an increase in surface hydrophobicity. There is a genuine need to design more selective flotation reagents, such as surfactants that chemisorb on specific minerals. There is also a need for development of chemical reagents such as flocculants, dewatering aids, stabilizers, etc.

It is perhaps useful at this stage to briefly mention the reagents usually used in coal benefication. Reagents are named according to their use although one reagent may have more than one application. Chemicals which bring about selective bubble attachment to particular mineral species are collectors e.g. kerosene, fuel oil, organic derivatives of ammonium hydroxide (32,33). Frothers are used to produce a moderately stable froth e.g. MIBC (4-methyl-2-pentanol), pine oil, cresol, cresylic acid. Modifying agents are used in numerous ways to enhance flotation. Modifiers may take the form of pH regulators, e.g. H⁺, OH⁻ ions, activators or depressants e.g. lime for pyrite depression, dextrin for coal depression. Flocculants, e.g. polyacrylamides, starch,

are used to produce coal flocs which settle rapidly and hence improve the "black water" problem.

I.7 Surfactants

Any compound collecting at an interface and changing the properties of that interface might be called a surfaceactive agent. Surfactants are amphiphilic molecules, containing both lyophobic and lyophilic groups. Many surfactants in solution associate above a certain critical concentration (termed the CMC) to form large molecular aggregates called micelles. The term normal micelles is used to refer to aggregation in aqueous media at relatively low concentrations. Surfactants are classified (1) nonionic, (2) catonic, (3) anionic or (4) amphoteric.

Nonionic surfactants in practical use are chiefly polyoxyethylene and polyoxypropylene derivatives. Generally, the polyoxyethylene types are of the form, R-O- $(CH_2-CH_2-O)_n$ -OH where R is alkyl or aryl. Because nonionic surfactants do not ionize in aqueous solution, they have many advantages as emulsifiers, detergents, wetting agents and for chemical studies. The inverse temperaturesolubility relation of polyoxyethylene surfactants, indicates that the overall solubility of these materials depends on the extent of hydration of the hydrophilic moiety. The water molecules interact with the ether oxygens by hydrogen bonding. Consequently, depending on the nature of the hydrophobic group, at leas four to-six ethylene

oxide units per molecule are required to produce a watersoluble surfactant.

Ionic surfactants have the combined properties of both non-polar and polar groups. Both the non-polar hydrocarbon chain and the polar ionic head determine the physical and chemical properties of the surfactant. Naturally, the character of the ionic head determines the sign of the charge on the surfactant ion. The size of the polar part is important since it determines the closeness of approach e.g. to an adsorbent's surface. The ionic head also determines whether the surfactant is a strong electrolyte, which completely ionizes in solution, or a weak electrolyte which ionizes only slightly and which hydrolyzes in solution to form a neutral molecule (34). While the charged head has an affinity for water, the nonpolar hydrocarbon is hydrophobic. The length of the hydrocarbon chain determines the degree of hydrophobicity and the critical micelle concentration (CMC), the longer the chain the more hydrophobic it is in character and the lower the CMC.

Surface active molecules have been characterized by an HLB number decribing the hydrophilic-lipophilic balance (35,36). The HLB number was designed as an empirical scale to be a guide toward predicting the emulsifier capacity of a compound and despite extensive application (36) remains an empirically defined quantity. Table 1.5 shows a few typical surfactants and some of their properties.

Table I.7

Properties of a few surfactants (37,38,39).

Name	Туре	General Formula	Average EO groups n	Nol. CMC. Wt. (M)	Solubility in water at room temperature	
Triton X-45	nonionic	2	5	427	dispersible	
Triton X-114	*	$C_{8}H_{17} \rightarrow (OCH_2CH_2)_{n}OH$	7-8	537 [*] 2 x 10 ⁻⁴	8	Ş
Triton X-100	n#	• = · •	9-10	∯ 625* ∘9 × 10 ⁻⁴	miscible	
DTAB	cationic	$C_{12}H_{25}(CH_3)_{3}(N)^{+}Br^{-}$, ÷ .	$308.3 1.4 \times 10^{-2}$	soluble '	8
DPC		~N ⁺ -C ₁₂ H ₂₅ C1 ⁻	-	283.9 1.4 x 10^{-2}	soluble -	
трв	n	$\sum_{n^{+}-c_{14}H_{29}Br^{-}}$	-	$356.4 \ 2.9 \times 10^{-3}$	н	
нрв 🖣	-	$\sqrt{2}N^{+}-C_{16}H_{33}Br^{-}$	-	384.5 (6-8)×10 ⁻⁴	R	
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Triton is a trade name of the Rohm and Haas Co., Philadelphia, Pa. DTAB - dodecyltrimethylammonium bromide DPC - dodecylpyridinium chloride TPB - tetradecylpyridinium bromide HPB - hexadecylpyridinium bromide

*average molecular weight

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I.8 <u>Research</u> Objective

Because of the above-mentioned problems of coal preparation, the general purpose of this dissertation is to contribute to an understanding of the colloid chemical criteria which underly efficient methods for coal beneficiation. Improvements in the beneficiation process may be derived from an increased knowledge of the mechanism of the alteration of the coal surface by the adsorption of various hydrophobic, hydrophilic, or amphiphilic substances. A survey of the literature reveals that such mechanisms are not adequately understood.

An important beginning towards realizing a solution to this problem, and recognizing that coal-fines and ultra-, fines will be an important product stream in any beneficiation process, is to study the surface characteristics of the coal water interface. As a result, ^b the objectives of this research are to study (1) the adsorption of organic molecules and simple surfactants from aqueous solution on coal surfaces and (2) the electrokinetic properties of coal particles in the presence of various electrolyte- and surfactant solutions. Electrokinetic properties of coal were determined in the presence of (1) salt solutions (2) nonionic surfactants and (3) cationic surfactants. In the coal-surfactant systems, the adsorption and the electrokinetic potential of coal were both studied as a function of solution concentrations and as a function of pH.

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Specific electrokinetic methods used were microelectrophoresis for the -200 mesh coal and streaming potential measurements for the larger -28 +35 mesh coal. The relationship between the zeta potential measured by these techniques and the adsorption isotherms is discussed. From the results of the effect of electrolytes and surfactant on the surface charge of coal, we discuss ,for example, the nature of the potential determining ions, points of zero charge (isoelectric points), and interaction between ions and surfactants and the coal surface.

1.9 Limitations of the research

According to the objectives of this thesis, this investigation is designed to establish the behavior of the coal-aqueous interface in the presence of salt and surfactant solutions. The interaction of molecules with a coal surface is a complex phenomenon influenced by several variables related to the characteristics of the coal surface as well as the nature of the adsorbate. The very nature of the coal surface is strongly influenced by its history and each individual coal possesses varying properties which depend on the coalification process. In addition, coals are usually porous, with pore size distribution varying from one coal to another. This can obviously affect the adsorption of various reagents since the surface in the pores may or may not be available to the adsorbate. Thus the determination of the actual surface area of coal from adsorption data is limited to the active sites available on the coal surface.

In spite of this, knowledge of the fundamental mechanism of adsorption on coal surfaces may be useful in understanding the role of added reagents in various separation processes.

I.10 Conclusion

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It is evident that in any study of coal-water interfaces, one should be aware of the associated problems as discussed in the previous sections. It is generally felt that more work is needed in the area of coal-surface active agent interactions and a study of adsorption of these molecules must be correlated with other interfacial properties such as electrokinetic potential, contact angle .etc. The next chapters address some of these problems.

Chapter II presents the theoretical foundations and the relationships and concepts which will be of considerable importance throughout the thesis. Chapter III outlines the experimental techniques used in this research, including a novel method of direct free catonic surfactant determinations in adsorption studies. The literature concerning adsorption on coal surfaces is discussed in Chapter IV. This chapter discusses a mechanism for the adsorption of the various molecules on coal and the chainlength dependence of the surfactants on the adsorption. Surface areas and free energies of adsorption
are also reported. Chapter V reports the effect of added electrolyte and surfactant solutions on the electrokinetic potential of coal as determined by microelectrophoresis. In this chapter, based on the electrokinetic and adsorption isotherms, a mechanism of coal-surfactant is suggested and compared to the results obtained for mineral-surfactant systems. Finally, in Chapter VI, a preliminary investigation of the streaming potential of larger coal particles in the presence of electrolyte and surfactant solutions is described. This study provides a basic look at surface properties of coal obtained by a different electrokinetic technique on a different size particle.

THEORY OF COAL-SOLUTION INTERFACE

CHAPTER II

II.1 General Introduction

From the discussion in Chapter I it is apparent that in order to beneficiate coal, it 'is necessary to study the, surface properties of coal in the presence of various surface modifying reagents. Surfactant molecules in a water-solid system are greatly influenced by a combination of hydrophobic and double layer effects. Adsorption of surface active agents at mineral-water interfaces are controlled in many cases by both of these effects. Similarly, the electrical double layer influences the nature of the adsorption isotherms, zeta potentials, "mode" of adsorption of certain species, etc., of charged colloidal systems. As a result, we will give a brief overview of the diffuse double layer theory, adsorption and electrokinetics theories. This is a necessary first step towards interpreting many of the experimental observations concerning the adsorption and electrokinetic properties of coal-water systems in the presence of surface active . agents. The double layer theory will then be used to develop a theory for surfactant adsorption on mineral surfaces. The description will be based on review articles of Overbeek, Grahame, Giles and texts (40-48).

II.2 The diffuse double layer

Several models have been proposed to explain double layer phenomena. Helmholtz's (49) and Perrin's (50) very important theoretical approaches to electrokinetics, although long recognized as inadequate, were the first attempts to explain the electrical double layer. These elementary ideas were later modified by Gouy (51) and Chapman (52) who introduced the concept of a diffuse ionic atmosphere. A pictorial representation of the diffuse double layer, generally used at present, is seen in Figure II.1. The treatment of the diffuse double layer rests on the Poisson and Boltzmann equations.

The Poisson equation relates the potential, ψ , which varies from ψ_{Q} at the surface to zero in the bulk solution, to the dielectric constant, ε , and charge density ρ at any point, at a distance of x from the surface, in the medium:

$$\nabla^2 \psi = -\rho/\epsilon \qquad (II.1)$$

(II.3)

For infinitely flat surfaces, the Laplacian operation becomes d^2/dx^2 . The distribution of ions in a potential field is given by

$$c_i = c_{i=0} \exp(-z_i e_{\psi}/kT)$$
 (II.2)

The charge density at any point is given by

$$-\rho = \sum_{i} z_{i} ec_{i}$$

Combining equations (II.1), (II.2) and (II.3) yields, for

Figure II.1. Illustration of the distribution of charge at a charged solid.



a z-z electrolyte, the equation

$$d\psi/dx = -(2c_{i,0}kT/\epsilon)^{1/2} [exp(z_i\psi/2kT)]$$
 (II.4)

where the negative root is taken so that $|\psi|$ decreases to zero in the bulk solution.

An approximation valid for small surface potentials, ψ , yields from equation (II.4)

$$\psi = \psi_0 \exp(-\kappa x) \tag{II.5}$$

where $\kappa = (2e^{2}\Sigma c_{i,0} z_{i}^{2}/\epsilon kT)^{1/2}$ (II.6) Since κ^{-1} has the dimension of length and is the value of x over which ψ drops to 1/e of ψ_{0} , it is often referred to as "the thickness of the double layer". For water at 25°C,

 $\kappa = 3.288 \text{ } \text{I}^{1/2} \text{ } \text{nm}^{-1}$ (II.7)

An increase in salt concentration reduces κ^{-1} and hence compresses the diffuse double layer.

The above equations have been derived on the following assumptions

1. the ions are point charges

2. the dièlectric permittivity is constant

3. the energy of an ion is the electrostatic energy of the average ion-field interaction.

It was soon recognized (53) that the assumptions, in particular neglecting the ionic dimensions or the hydrated ion dimensions, cause these equations to predict impossibly high concentrations near the charged surface. Much of this

discrepancy was explained by Stern (53). He noted that the ions comprising the double layer have finite sizes and so cannot approach one another and the surface as closely as assumed in the Poisson-Boltzmann approach. He further recognized the existence of specific ion adsorption, based on the Langmuir theory (54,55) of monomolecular adsorption. The Stern model in brief, defines a region adjacent to surface of width & (approximately a single ion in thickness); in this region there is a sharp fall in ' potential from ψ_0 to ψ_s . The diffuse double layer can be thought to begin at x = δ with " ψ_0 " = ψ_s . In this diffuse atmosphere, the adsorption forces and finite dimensions of the ions are neglected, so that the Gouy-Chapman theory is applicable. Figure II.2 shows a typical variation in potential using the Gouy-Chapman model ((a)) and the Stern model ((b)).

More elaborate models have been proposed by others (56-58). Nevertheless, the notions developed by Gouy and Chapman made it possible to explain the difference between the thermodynamic ψ_0 and the electrokinetic ζ potentials and to discover the cause for some of the experimentally established relationships of electrokinetics which will be discussed in the later sections of this chapter. On the concept of electrokinetic potential, Guggenheim (59) pointed out

"Most authors instead of using Helmholtz's (49) strength of the double layer here denoted by τ prefer to consider another quantity

Figure II.2. Diagram of variation of potential with distance (a) Gouy-Chapman model (b) Stern model. ψ_0 , surface potential; ψ_{δ} , Stern potential; ζ zeta potential. -.- Stern plane; -- Shear plane.

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introduced by Perrin (50) and subsequently denoted by z by Freundlich (60). It is derived from τ by division by the rational permittivity. In the author's opinion the introduction of this subsidiary quantity adds nothing except unneccessary complication!"

II.3 Adsorption at the solid-solution interface

Adsorption from solutions is usually characterized by a competition between the solute and solvent for the available adsorption sites on the solid. There are several excellent reviews of this phenomenon in the literature (42,44,61-66). The adsorption isotherm, i.e. a plot of the amount of adsorbate adsorbed per unit weight of solid (or area if known) versus the final equilibrium bulk concentration of the adsorbate, is the most convenient form to plot experimental data and to develop theoretical treatments. Several shapes of the adsorption isotherms of solids from solution have been observed and these have been classified by Giles (42). In studies of adsorption from this type of system, the following aspects have emerged as being of greatest interest and importance (61):

- (i) the shape of the adsorption isotherm and the possibility of fitting it with an appropriate equation,
- (ii) the significance of the adsorption limit or the plateau found in most isotherms,
- (ili) the extent to which the solvent is adsorbed,
 (iv) a consideration of whether adsorption is confined
 to a single molecular layer or extends over several

layers,

(v) the orientation of the adsorbed molecules,

(vi) the existence of both physical and chemical adsorption.

In addition, the measurement of the specific areas of solids, is becoming increasingly important and a wide range of methods is now available (67). Adsorption is useful for solids of relatively high specific surface area, for example finely divided solids. Methods based on physical adsorption of gases (nitrogen, argon, krypton) at low temperatures are as near to being standard methods as we have. Because of this, the use of adsorption from solution in determining surface areas is of secondary importance. Nevertheless, for a method based on adsorption from solution to be sound, Kipling (61) suggests that two fundamental requirements must be fulfilled: (1) it should be postible to determine the conditions under which a complete monolayer of a given component is formed on the solid (2) it is necessary to assign an accurate value to the area occupied by the adsorbed molecular species; this normally means that the orientation of the adsorbed molecules must be known with confidence.

To summarize, it seems that there is no general equation which can be relied upon to give extremely accurate data of surface areas of porous solids especially minerals possessing various functional groups as part of their inherent structure. In such cases, different

adsorbates will adsorb differently on the solids yielding different surface areas. Moreover, the fact that the observed data can be fitted by a particular equation does not mean that the constants of the equation are necessarily related to the monolayer. However Sing (65) recommended that the terms Langmuir or BET area be used where appropriate, with a clear indication of the range of linearity of Langmuir or BET plot and the magnitude of the various constants so obtained from the plot. As such, a suitable solute can be used for surface area determinations of solids from adsorption from solutions. Giles (42,68) defined the characteristics of such a solute and although he found no single substance to meet all the requirements," he met with considerable success in using p-nitrophenol (68) on finely divided solids such as ceramic, carbon, coal.

II.3.1 Characteristics of adsorption from solution

The experimental measurement in adsorption from solution is the change in concentration of the solution from which molecules are adsorbed. There is always competition among the solute and solvent of the solution for the available adsorption sites. The degree of adsorption can be determined by making use of the standard Gibbs equation and from the following material balance:

$$n_i^s = n_i - n_i' \qquad (II.8)$$

If it is assumed that component 2, i.e. the solvent, is not

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adsorbed then equation (II.8) can be written as

$$n_i^s = V_{\text{solution}} (c_i^o - c_i)$$
 (II.9)

From equation (II.9) it can be seen that it is relatively easy to measure the amount adsorbed by monitoring the bulk solution concentration. Because of the case in which n_i^s is determined as a function of bulk concentration, the results of studies of adsorption on solids are presented in the form of adsorption isotherms i.e. plots of amount of solute adsorbed versus the final equilibrium bulk concentration.

II.3.2 The Langmuir isotherm

The derivation of the Langmuir equation is based on the assumption that the adsorption rate is proportional to the bulk concentration of the adsorbate and the number of vacant adsorption sites on the solid surface, while the rate of desorption is proportional to the number of adsorption sites occupied by the adsorbate. At equilibrium the adsorption and desorption rates are equal so that for a one component system the degree of surface coverage, x/x_m is related to the concentration of the adsorbate in the bulk solution by

$$x/x_{m} = K_{eq}c / (1 + K_{eq}c)$$
 (II.10)

which is the form in which the Langmuir isotherm is often written. For the convenience of testing data, the isotherm is easily linearized to give

$$c/x = 1/K_{eq}x_{m} + c/x_{m}$$
 (II.11)

A plot of c/x against c should yield a straight line and values of x_m and K_{eq} can be determined. In turn, x_m is related to the area of the adsorbent by

$$x_{\rm m} = \Sigma / L \sigma^0 \qquad (II.12)$$

The standard free energy, ΔG° , in the case of adsorption from solutions, characterizes the work of transfer of the molecules of the sorbate from the bulk phase of the solution to the surface of the adsorbent and is given by

$$\Delta G^{O} = -RT \ln K_{eq} \qquad (II.13)$$

The basic assumptions involved in the derivation of the Langmuir isotherm include (i) no lateral interactions between the adsorbed molecules (2), a homogeneous surface (3) no formation of a multilayer and (4) a reasonably long residence time of a molecule on the surface.

Other methods used to describe adsorption from solution include the Freundlich and the BET isotherms. The Freundlich isotherm is generally used for heterogeneous 'surfaces while the BET takes into account the concept of multilayer adsorption. The Freundlich equation, unlike the Langmuir one, does not become linear at low concentrations but remains concave to the concentration axis; nor does it show saturation or limiting value. Furthermore if data fit the Freundlich equation it is only likely, but not proven that the surface is heterogeneous. On the other hand, the

Langmuir equation applies to a large number of adsorption A plot of c/x, against c, should yield a systems (45). straight line, but in some systems, an apparently nonlinearity in the linearized Langmuireplot occurs. This might be an indication of preferential adsorption at the more active sites of a heterogeneous adsorbent surface. In such a case, the choice of slope i.e. at low concentration or over the total concentration range of the linearized Langmuir isotherm usually depends on the range and spread of the data and, on the particular datum points to be emphasized. Adsorption on coal surfaces has been reported using both the Freundlich isotherm (69-71) and the Langmuir isotherm ~(72-75).

II.4 Electrokinetic phenomena

Electrokinetics is the general description applied to the four phenomena which arise when the solution and electrical double layer move relative to the solid surface. These effects may arise either from an external electrical field directed along the phase boundary resulting in a movement (electroosmosis, electrophoresis) or from a movement of phases along each other, resulting in a transport of charge (streaming current, streaming potential, sedimentation potential). In each of the electrokinetic phenomena, a slip plane between the charged surface and the medium is involved. The electric potential at this "plane of shear" between an assumed fixed layer

directly adjacent to the particle and the liquid constituting the bulk solution determines the electrokinetic phenomena and is called the zeta potential, ζ . The location of the slipping plane is not too well defined. Early estimates of the position of the plane of shear are well documented in the literature (76-78) for example, Overbeek (77) suggested that the slipping plane was situated in the Stern layer, in the diffuse layer, or just in the transition plane between the two (Figure II.2 (b)).

Any theoretical treatment of electrokinetics must start from the fundamental equations describing (1) the electrostatic potential (2) the fluid flow and (3) the ionic current flows which are generated by the relative motion of the phases. The following subsections discuss the classical theoretical treatment of the two electrokinetic techniques used in this research and some general refinements. A detailed treatment is given by Overbeek (40) and Dukhin and Derjaguin (47). Section II.5 will discuss the relations between the various electrokinetic phenomena using the model of irreversible thermodynamics rather than the double layer model.

II.4.1 Electrophoresis

Electrophoresis is the process in which the application of an electric field causes the motion of, perticles through a liquid. One of the most commonly applicable forms of the zeta potential-mobility

relationship is the Helmholtz-Smoluchowski equation (49,79). The derivation of this equation is based on the following considerations. When an electric field X is applied parallel to a flat nonconducting surface, each layer of liquid will rapidly attain a uniform velocity parallel to the surface with electrical and viscous forces balanced. Equating the electrical and viscous forces on a liquid layer of unit area, thickness dx, distance x from the surface and having bulk charge density ρ ,

$$X \rho dx = (\eta dv/dx)_{x+dx} - (\eta dv/dx)_{x} \qquad (II.14)$$

Inserting the Poisson equation (II.1) / and integrating with the boundary conditions, at $x = \infty$, $d\psi/dx = 0$ and dv/dx = 0, 0), ε and η are constants yield

$$-X \varepsilon \psi = \eta v + \text{constant}$$
 (II.15)

The boundary conditions for electrophoresis and $\psi = 0$, v = 0 at $x = \infty$ and $\psi = \zeta$, $v = -v_e$ at the surface of shear. Equation (II.15) becomes

$$u_e = v_e/X = \epsilon \zeta / \eta$$
 (II.16)

The approximations implicit in this equation are (i) the particle is non-conducting (ii) the radius of curvature is large compared with 1/k (iii) the viscosity and dielectric constants are constant and (iv) the distribution of the charges in the ionic double layer is not affected by the applied field. At 25 °C, equation

(II.16) becomes

 ζ (in mV) = 12.8 x u_e (in µm cm V⁻¹ s₂)

(II.17)

II.4.2 Streaming potential

. Streaming potentials were first introduced by Quincke (80) (quoted in (47)). The effect is based on the following considerations. When a liquid is forced through a capillary or porous plug by application of pressure, the charges in the mobile part of the double layer are carried towards the end. This constitutes a streaming current. As a consequence of this transport of charge a potential difference arises between the ends of the capillary or plug, which causes a conduction current through the capillary directed oppositely to the convection or streaming current. In the stationary state, the convection current, which is proportional to the pressure difference P, counterbalances the conduction current, which is proportional to the potential difference or streaming potential, E. As a result, the streaming potential is related to the pressure difference by the equation (40,46)

 $E/P = \varepsilon \zeta / \eta \kappa$ (II.18)

In aqueous systems at 25 °C, equation (II.20) becomes

 ζ (in mV) = 9.69 x 10⁴ E κ /P (II.19) measuring E in millivolts, κ in ohm⁻¹ cm⁻¹ and P in cm of Hg. A plot of E versus P should yield a straight line. Conditions which are to be satisfied for the validity of equation (II.18) are

(1) the flow of the liquid must be laminar,

(2) the pore size of the plug must be much larger than the thickness of the double layer,

(3) the conductance determining the conduction current should depend solely on the bulk conductivity of the liquid. The surface conductance should not play a part of any importance. If this condition is not fulfilled, corrections can sometimes be applied (78).

II.4.3 <u>Restrictions on the use of electrokinetic equations</u>

Some important phenomena that restrict the use of equations (II.16) and (II.18) in determining the zeta potential are (i) relaxation effect (ii) Brownian motion (iii) viscoelectric effect and (iv) surface conductance. These effects have been discussed in detail by Overbeek (40,81,82), Booth (83,84), Henry (85) and others (44,46,86). They will only be briefly examined here.

Mickel (87) obtained a significantly different result from equation (II.16) for the determination of the zeta potential of a spherical particle. Briefly, the derivation of the equation is based on the following considerations:

(1) a is small enough for the spherical particle to be treated as a point charge in an unperturbed field.

(2) the particle is, nevertheless, large enough for . Stokes' law to apply.

By balancing the electrical force on the particle against

the Stokes functional resistance we obtain

$$QX = 6 \pi \eta a v_e \qquad (II.20)$$

$$u_{o} = v_{o}/X = Q/6\pi\eta a$$
 (II.21)

The zeta potential on the particle is given by

$$Q = 4 \pi \varepsilon_a \psi (1 + \kappa_a)$$
 (II.22)

Substituting equation (II.22) in equation (II.21) we get .

$$u_e = 2 \varepsilon \zeta (1 + \kappa a)/3$$
 (11.23)

Since $\kappa a << 1$, equation (II.23) becomes

u_e = 2°C/3 n The apparent contradiction between equations (II.16) and (II.24) was resolved by Henry (85). Henry showed that when an external field was superimposed on a local field around a particle, the mobility could be written as

(11.25)

 $u_{\rho} = (2 \epsilon \zeta / 3) f(\kappa a)$

where κ is given by equation (II.6) and a is the radius of the particle. In the limiting case $\kappa a >>1$ (i.e. when the double layer is small compared to the radius of the particle), $f(\kappa a) = 3/2$ and Henry's equation(II.25) is reduced to the Helmholtz-Smoluchowski equation (II.16). When $\kappa a <<1$, $f(\kappa a) = 1$ and equation (II.25) is reduced to equation (II.24). Equation (II.24) is not likely to be applicable to particle electrophoresis in aqueous media;

for example $\kappa a = 0.1$ would mean that the radii of particles suspended in an aqueous 1-1 electrolyte solution of concentration 10^{-4} M would be about $3nm(i.e. <<1\mu)$. The radii of the coal particles used in this study are much greater than 100nm and as such the use of equation(II.16) is valid in calculating zeta potential barring other effects.

The superimposition of the applied field and the field of the double layer leads to a mutual distortion of each field. The relaxation effect is a result of the finite time required for the original symmetry of the double layer to be restored in a moving system. The result of this effect causes a velocity reduction of the migrating particle. Because of mathematical difficulties, calculations of the relaxation effect are difficult and the validity of the results is rather restricted (81-85). In general, the relaxation effect is negligible for large and small values of a i.e. for $\kappa a > 1000$ or $\kappa a < 0.01$ (81,82). In effect, equation (II.16) remains valid, irrespective of the shape of the particle, if relaxation is taken into account for $\kappa a > 1000$.

In electrophoresis, the motion of the colloidal particle in the direction of the field is superimposed on its Brownian motion. Wiersema (88) suggested that the Brownian motion correction is negligible in most practical cases. The presence of an electrical double layer exerts a profound influence on the flow behavior of a fluid. The

electric field strength close to the shear plane can be high enough to significantly affect the ratio n/ϵ by dipole orientation. All such influences are grouped together under the name of electroviscous effects. As a result of the flow of a liquid, under a pressure gradient, through a capillary or porous plug, the liquid appears to exhibit an enhanced viscosity. A similar effect, occurs when a dilute suspension of colloidal particles is sheared. Lyklema and Overbeek (77) concluded that the effect of the electric field - strength on the dielectric constant was insignificant but its effect on the viscosity might be significant. Hunter (46) discusses these effects and their contribution to the calculation of the zeta potential. In brief, the most practical approach seems not to take the viscoelectric effect into account (88). The influence of the surface conductivity of the colloid particle has been discussed in several reviews (47,82,85). It is generally concluded that no surface conductance correction should be applied when the relaxation correction has been found to be negligible . (i.e. for spherical particles and $\kappa a \ll 1$ or $\kappa a \gg 1$).

To summarize the discussion in this section, it appears as if the simple model in calculating zeta potential based on equations (II.16) and (II.18) has a wider range of application than one might expect. One of the reasons is that some of the complications are quite negligible or can be avoided experimentally without much trouble. In any case, nearly all studies on the zeta potential of

particles whose sizes are greater than that of colloidal particles(> 1μ) use the simple Smoluchowski equation (46,69-71,73-75).

II.5 Irreversible thermodynamics

Absolute tests of the equations developed in Section II.4 are not available because there is no independent measurement of the electrokinetic potential. The equations in Section II.4 were based on the double layer model. It can be demonstrated that the relations between the electrokinetic phenomena are generally valid and independent of the chosen model. Such relations can be discussed conveniently using the theory of the thermodynamics of irreversible processes, as founded by Onsager (89) and developed by Prigogine (90), de Groot (91) and applied to membrane phenomena by Staverman (92,93).

The theoretical analysis is based on an expression for the rate of entropy production which is a trademark of irreversibility. The entropy production per unit time for an irreversible system must be written as a function of the fluxes of the components and the conjugate thermodynamics which give then

$$d(\Delta s)/dt = \sum J_i X_i$$
 (II.26)

where J_i are the fluxes and X_i are the forces. The most general expression for the macroscopic laws or phenomenological equations assumes that every force influences a flux and considering only states close to

equilibrium, we can relate the fluxes to the forces through linear phenomenological equations of the form

$$\mathbf{J}_{\mathbf{i}} = \Sigma \mathbf{L}_{\mathbf{i}\mathbf{j}} \mathbf{X}_{\mathbf{j}}$$
(11.27)

where i,j = 1,2,3,...,n for a system of n components. The L_{ij} are the phenomenological coefficients, which according to the Onsager reciprocal relation are interrelated

$$L_{ij} = L_{ji}$$
 (i * j, i, j = 1, 2, 3, ... n) (II.28)

Although equation (II.28) has a general validity, it is restricted to systems not too far from equilibrium. These ideas can be applied to electrokinetics to show that certain electrokinetic phenomena are quantitively interrelated by reciprocal relations.

Consider a system, containing n (i = 1,2,...n) components carrying electrical charges and enclosed in a reservoir which contains two vessels connected by a porous plug and in each reservoir is situated an electrode. Such a system can be described in terms of two fluxes and two forces. The forces are the electrical potential, E, and the pressure gradient, P, while the fluxes are the current, I, and the volume flow, V. The rate of entropy production can be determined by considering the energy dissipation as produced by the sum of IE and VP

$$T(dS_{i}/dt) = VP + IE$$
 (II.29)

The phenomenological equations are

I	=	L ₁₁ E	+	L ₁₂ P	•	ч	(11.30)
V	=	L ₂₁ E	+	L ₂₂ P			(11.31)

Volume flow is in principle not conserved. However, the general equations give species fluxes, which can be related to volume flows, current, etc. as in equation (II.29) (94).

In the absence of an electric field (E=0) equation (II.31) reduces to

$$L_{22} = (V/P)_{E=0}$$
 (II.32)

from which we have according to Poiseuille's law

$$L_{22} = r^2/8\eta$$
 (II.33)

Streaming potential is defined a the potential difference, E, generated by a pressure difference, P, in a stationary state with zero electric current. From equation (II.28)

$$(E/P)_{I=0} = -L_{12}/L_{11}$$
 (II.34)

Electroosmosis is defined as the flow of matter or volume flow, V, per unit electric current in a state of uniform pressure. From equation (II.30) and (II.31) we get

$$(V/I)_{P=0} = L_{21}/L_{11}$$
 (II.35)

From the Onsager relation and equations (II.34) and (II.35) we get

 $(E/P)_{I=0} = -(V/I)_{P=0}$ (II.36) In the absence of a pressure gradient, equation (II.30) becomes

 $L_{11} = (I/E)_{P=0}$ (II.37)

which is just the electrical conductivity.

Other similar relationships for example electroosmotic pressure, streaming current can be determined. Equation (II.36) is known as Saxen's relation and shows that the electroosmotic volume flow is equal to (although opposite in sign) to the streaming potential. It can be shown that the coefficient $L_{12} = L_{21}$ is closely related to the strength of the electric double layer, τ , by the equation

 $L_{21} = \tau / \eta$ (II.38)

Non-equilibrium thermodynamics has established general relations which cannot be invalidated by complications of surface conductance, tortuosity, etc. and as Guggenheim (95) quite succinctly states

"The essential consequence of Onsager's relation is this. All the electrokinetic effects require for their quantitative description a knowledge of the electric conductivity, the viscosity and <u>one</u> <u>other</u> coefficient not two."

CHAPTER III

EXPERIMENTAL

III.1 Materials

Coal fines selected for this study were from the -28 mesh fines circuit of the Victoria Junction Wash Plant of the Cape Breton Development Corporation, Glace Bay, Nova Scotia, Canada. The coal treated in this plant is a highly volatele bituminous coal from the Harbor Seam. Because of the hydrophobic nature of the coal treated in this plant, no collecting agents have to be added in the flotation unit. Thus the coal has only been in contact with relatively low 4-methyl -2-pentanol, (MIBC) concentrations, not with oil or kerosene. The fines collected after flotation were dry ground and sieved. The -28 + 35 mesh (-425 + 600 μ m) and the -200 mesh (<75 μ m) portions were collected and evacuated at room temperature for 4 days prior to surfactant adsorption- or electrokinetic studies.

Phenol, p-nitrophenol (Fisher Scientific) and Triton X-100 (Rohm and Haas), a widely used commercial product consisting of a mixture of octylphenol polyethoxylates with an average of 9-10 ethylene oxide groups per molecule, were used without further purification. Dodecyltrimethylammonium bromide, DTAB, (Kodak Laboratory Chemicals), dodecylpyridinium chloride, DPC, (TCI Chemicals, Japan), tetradecylpyridinium bromide (96), TPB, and

hexadecylpyridinium bromide, HPB, (Kodak Laboratory Chemicals) were purified by repeated recrystallization from ethanol/acetone. Sodium dodecylsulfate, NaDS, used in preparing the membrane electrodes, was prepared from dodecylalcohol purified by fractional distillation through esterfication with chlorosulfonic acid (97). Poly(vinylchloride) (PVC, high molecular weight, Aldrich), bis(2-ethylhexyl) phthalate (GR, Aldrich) and tetrahydrofuran (AR, BDH Chemicals) were used without further purification. Analytical-grade sodium chloride was also used without further purification.

III.2 Analysis of coal samples

Both proximate and ultimate analysis of the coal used in this research were carried out. Proximate analysis determines the moisture, volatile matter, fixed carbon (by difference) and ash in the coal. Ultimate analysis gives the percent carbon and hydrogen in the sample, as found in the gaseous products of its complete combustion, the percent sulfur, nitrogen and ash in the material as a whole and the percent oxygen by difference. The methods of analysis are well documented by The American Society for Testing Material, A.S.T.M. (98) and by Montgomery (99). The fuel ratio was calculated from the equation

Fuel Ratio = % volatile matter / % ash (III.1) and the fixed carbon from the equation Fixed carbon = 100- (% ash + % volatile matter + % moisture) (III.2)

III.3 Principle of surfactant ion selective electrode

A recent study of a number of surfactant ion selective membrane electrodes (100-104) has shown the utility of such electrodes in e.g. the determination of critical micelle concentrations as well as in potentiometric titration. In addition, the use of surfactant ion selective electrodes has made it possible to obtain information regarding the surfactant ion activity in solution of ionic surfactant of low concentration and in the presence of added salt (101,103).

The potential across a membrane separating two solutions containing electroactive ions, i, and interfering ions, j, which can be transported across the membrane is commonly represented by the equation of the form (100)

$$E = E_a - (RT/nF) [ln {(a_i + K_{ij} a_j)/a_i^0]]$$
 (III.3).

According to the theoretical treatment of membrane potentials (100-104), the selectivity coefficient is a function of the mobility of the primary ion, u_i , and the partition coefficient, k, between the membrane and the bulk solution. In the case of the liquid membrane, K_{ij} is given by (100)

$$\kappa_{ij}^{\text{pot}} = u_{jkj}/u_{iki}$$
(III.4)

Surfactant ions are soluble both in water and in the organic phases such as organic liquin and plasticizers while inorganic ions are less soluble in the organic phase.

This means that the partition coefficient of the surfactant ions, k_i , between water and organic phases is much larger than that of the partition coefficient, k_j , of inorganic ions, As a result, organic liquids or plastic membranes which are immiscible with water can be used as surfactant ion selective membranes. Some surfactant selective electrodes have been developed which make use of this difference in solubility, and these electrodes have been applied to the study of surfactant solution chemistry and surfactant adsorption (102, 105-108).

III.4 Methods of measurements

There are many reviews of the analysis of adsorption densities and surface charge in the literature (40,45,46,61,62,70). Some of the methods used to determine free surfactant concentration include refractometry, colorimetry, titrimetric analysis, the use of radioactive tracers and surface tension measurements. Electroosmosis, sedimentation potential, titration, and suspension effect have also been used to determine the electrokinetic charge on a solid surface. Only the methods used in this research will be discussed.

III.4.1 Adsorption measurements

The methods used to determine free solute concentration were (1) direct spectrophotometry and (2) emf measurements. Direct spectrophotometry is a convenient way of measuring surfactants with aryl groups in very small concentrations.

The free concentration of a surfactant in suspension can be determined from a calibration curve for the maximum ultraviolet absorption of the component of interest. Concentrations of ionic surfactants in colloidal or particulate suspensions can be determined by the use of a surfactant ion selective electrode. The electromotive force (emf) versus log concentration of free surfactant (c_s) can be used as a calibration curve at concentrations below the CMC.

The adsorption of various reagents on coal was determined by measuring the adsorbate concentration in solution before and after adsorption. pH was adjusted by addition of either 0.1 M HCl or 0.01 M NaOH. The suspensions were shaken at room temperature for a required time, usually 23 hours, after which they were centrifuged for 20 minutes at 10,000 rpm, removing all turbidity. The concentrations of the reagents were measured by the different techniques previously mentioned. In a number of cases the time dependence of adsorption was also studied.

III.4.1.1 Spectrophotometric concentration determination

The solid/solution ratio used was 0.50 g/30 cm³. Solution concentrations of phenol, p-nitrophenol, Triton X-100, DPC, TPB and HPB were determined by direct UV spectrophotometry at the wavelength of maximum absorption (269.9, 316.1, 278.0 nm for phenol, p-nitrophenol and Triton X-100 respectively and 259.1 nm for DPC, TPB and HPB) using a Cary 219 (Varian, Palo Alto, California)

spectrophotometer.

III.4.1.2 Potentiometric concentration determination

The solid/solution ratio used in these measurements was 1.00q/30 cm³. Free surfactant concentrations of DTAB, DPC I and TPB in solutions with pH values between 4.0 and 10.0 were determined by means of surfactant selective plastic membrane electrodes (106-108). The cation selective membrane was prepared from 23 wt% PVC, 76 wt % bis (2ethylhexyl) phthalate as plasticizer and 0.7 wt % carrier complex. The carrier complex used in this membrane was prepared by dissolving equivalent amounts of surfactant and NaDS. The resulting white precipitate was washed with water followed by recrystallization from acetone. A mixture of 0.35 g of PVC, 1.15 g of bis (2 - ethylhexyl) phthalate and 10 mg of carrier complex was dissolved in about 6 cm^3 of tetrahydrofuran by heating. The clear viscous solution was cast in a petri dish of 10 cm diameter. The solvent, tetrahydrofuran, was gradually evaporated off in air. A piece of the resulting poly (vinylchloride) membrane was glued to the bottom of a hard PVC tube by using a tetrahydrofuran solution of PVC as an adhesive (102). The carrier complex in the active membrane was changed for each different surfactant.

The membrane potential was measured with the following

cell calomel electrodelsatd. KCl solutionagar, 3m NH₄Cl 1 2 3 test solutionmembranelreference solutionlagar, 4 5 6 3m NH₄Cl satd. KCl solution calomel electrode (III.5) 7 8 9

where the reference solution was 0.001 m surfactant. The cell assembly is depicted in Figure III.1, where the numbers correspond to the numbers in electrochemical cell in III.3. The emf of the cell was measured by a Keithley 616 digital electrometer with a stability of 0.1 mV. The potential was monitored with a recorder. The electrode was tested for Nernstian behavior before and after use in the colloidal suspensions.

III.5 <u>Electrokinetics</u>

III.5.1 Electrophoretic measurement

Electrokinetic properties of the -200 mesh coal were determined by means of a microelectrophoresis technique. The mobilities of all solid were determined over a wide pH range in the presence of both salt and surfactant using both a Carl Zeiss Cytopherometer and a Rank Brothers Mark II Particle Micro-Electrophoresis Apparatus with TV monitor and rotating prism attachment. Both instruments contained a flat cell. 0.50 g samples of coal were added to 100 cm³ of surfactant solutions of known concentrations and pH. The samples were shaken at room temperature for 23 hours before measurement. All measurements were made in 1×10^{-4} in NaCl solutions.

III.5.2 Streaming potential measurements

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Zeta potentials of the -28 + 35 mesh coal were determined by streaming potential measurements. The streaming potential apparatus used in this investigation

Figure III.1. Schematic diagram of potentiometric cell assembly. Numbers correspond to numbers in equation III.5. E- digital electrometer; A and B- autoburets; H- pinhole Th- thermostat; MS- magnetic stirrer.



was essentially the same as that described by Campbel 1(30), Fuerstenau'(109) and Parreira (110,111). A schematic arrangement is given in Figure III.2. The heart of the apparatus is formed by bulbs (VL, VR) and cell (C). The cell consists of two 14/35 ground-glass joints, the ends of whichare closed off by platinum disk electrodes with holes drilled through them to permit passage of the solution. These electrodes were connected to a Keithley 600 B electrometer which is in turn connected to a Fisher "Recordall 5000 Series recorder to monitor the streaming potential. To facilitate the dismantling and reassembling of the equipment for cleaning, tygon tubing was use for most connections (labelled T in Figure III.2). The vacuum in bulb (B) pulls the liquid slowly through the cell with . the porous plug. The pressure under which the liquid is forced through the plug is measured by the manometer, M.

With the electrodes in place, the cell (C) was filled with -28 + 35 mesh coal by tapping to ensure proper packing. When the outer joint is full, the inner joint is inserted and the cell is reassembled into the apparatus. The bulb (VL) is filled with the solution to be studied at its natural pH (i.e. the pH of the solution containing only salt and surfactant) and left overnight to equilibrate. Streaming potentials, E, were then measured as a function of driving pressure, P. From a plot of E vs P, the slope of the straight line was obtained. The conductivity of the bulk solution was measured with an Industrial Instruments
Figure III.2. Schematic diagram of streaming potential apparatus. B- vacuum bulb; C- cell; E- Pt electrodes; ELelectrometer; M- oil manometer; R- recorder; T- tygon tubing; VL and VR- liquid bulbs.





(Cedar Grove, New Jersey) Conductivity Bridge. Streaming potentials were measured as a function of salt and surfactant concentration at different pHs. Once a solution of fixed concentration was left in contact with the porous plug overnight, solutions of similar concentrations but different pH were allowed to equilibrate for 1/2 hour before the measurements. This method has been found to produce reproducible results.

III.6 General conditions

£'H₂O, m)

All experiments were carried out at 25 ± 1 °C and at surfactant solution concentrations well below the critical micelle concentration (CMC) of each surfactant. The coalsurfactant suspensions were studied at natural pH (i.e. the pH of coal fines directly suspended in 10^{-4} m NaCl and/or surfactant) and under varying pH conditions. All aqueous solutions were prepared by weight from surfactant and sodium chloride stock solutions in distilled and deionized water. All concentrations are given as molalities (mol/kg

CHAPTER IV

ADSORPTION OF SURFACE ACTIVE AGENTS

IV.1 Introduction

Adsorption of appropriate additives at the solidliquid interface can control the surface charge and/or the hydrophobic-hydrophilic character of the surface. One or other of these characteristics, and often both, may be important in determining the wettability, the stability, flotability and the rheology of the system. In recent years, the role of surfactants and polymers at the coalwater interface has been the subject of considerable attention. Because of the natural hydrophobicity of coal (24), many amphiphilic molecules adsorb at the coal-water interface at very low amphiphile solution concentrations. Thus difficulty of measurement as well as problems with sample inhomogeniety and diversity in properties of different coals may be reasons for the relative scarcity of systematic investigations on adsorption at the coal-water The next section reviews the available interface. literature on adsorption from solution on coal surface.

IV.2 Review of related studies

The adsorption of electrolytes on active carbons has been rather thoroughly studied (61,66). In these investigations, a number of interesting principles have been reported concerning the adsorption of both strong and

weak electrolytes on active carbons. In contrast, only a small amount of research has been reported on the adsorption of electrolytes on coal surfaces. Most of the adsorption studies on coal have been done in the U.S.S.R., on Russsian coals. It should be noted that active carbons and coals are quite different with respect to porosity, surface functional groups, etc. and that results relating to the adsorption of a particular electrolyte on either surface can be very different. Nevertheless, some review of the adsorption on carbon surfaces is warranted since the mechanism of adsorption of similar electrolyte on both carbon and coal surfaces will be compared.

Wheeler and Levy (112) concluded that the adsorption of ortho-alkylated phenols on carbon from cyclohexane solutions takes place only at certain "active centres" on the adsorbent and that the hydroxyl group is largely responsible for the adsorption. Other research groups (113,114) reported that phenol adsorbs from aqueous solutions through interaction between the benzene ring and the carbon surface. Bennett and Abram (115) studied the adsorption of hexadecyltrimethylammonium bromide, HTAB, and Aerosol OT (di-2-ethylhexyl sodium sulfosuccinate) on carbon and bone char and concluded that the Aerosol OT adsorption from water gives the whole surface, while the HTAB adsorption gives the hydrophobic part of the surface.

Evanson et al. (116) have shown that phenol is

adsorbed considerably on low rank coals in a short period of time and that those coals are porous. Vlasova et al. (117) found that the adsorption on coal surfaces of naliphatic alcohols increases with the degree of oxidation. It was suggested that the adsorption of n-hexanol and nheptanol from aqueous solution on the surface of oxidized coal involves hydrogen bonding. The treatment of oxidized coals with alcohols makes their surfaces less hydrophilic. This effect is more pronounced as the alcohol carbon chain length is increased (the range studied was C_2-C_8). As a result, the flotation properties of the coal/alcohol entity is improved. The adsorption of phenol and n-hexanol from water on coals of different rank was found to take place through their hydrophobic moieties (21) with the hydrophilic parts oriented towards the aqueous phase. Also the free energy of adsorption was found to increase with the rank of the coal.

Shanter (118) studied the adsorption of acids, alcohols and esters from aqueous solution by coals and concluded that the molecules of these compounds are oriented with their apolar part toward the surfaces of coals of high and medium rank and with their polar moiety toward the surfaces of coals of low rank and also highly oxidized coal. Giles and Nakhwa (68) have concluded that the adsorption of p-nitrophenol from solution at room temperature is suitable for specific surface area measurements on a wide variety of solids, including carbon,

coals and fibres. Laskowski (119) suggested that the hydrophobic carbon part of a coal surface can be determined by the adsorption of the cationic surfactant, HTAB, from aqueous solution.

Basenkova and Zubkova (120) found that aniline adsorbs better on oxidized coal than on the initial, untreated coal of low rank but the adsorption is the same in both states for the lean, higher rank coal. It was concluded that the interaction of aniline from aqueous solution has a specific hature and probably takes place through functional groups. It was also found that the adsorption of propanoic acid and of 1-propanol and 2-propanol on "fat" (high volatile medium rank) run of the mine coal is smaller than that on "lean" (low volatile high rank) unoxidized coal. The explanation given was that these compounds are oriented with their hydrophobic ends to the coal surface and their polar ends directed towards the solution. BET surface areas of 0.8 m^2g^{-1} and 2.0 m^2g^{-1} were determined for "Zh" and "T" coals respectively, based on areas covered by nitrogen.

Kucher et al. (22) investigated the adsorption of a number of inorganic (HCl, H_2SO_4 , H_3PO_4) and organic (oxalic, malonic, succinic, adipic) acids on unoxidized and, oxidized Russian low ash (≈ 3 %) coals of various rank. It was found that the adsorption of the inorganic acids on the oxidized coal was much less than on the original unoxidized coal and in the order

 $HC1 > H_2SO_4 > H_3PO_4$

It was suggested that this decrease in adsorption with increase in molecular weight of the inorganic acids was probably due to anion adsorption in addition to H+ adsorption and that the adsorption from aqueous solutions of strong inorganic acids on the coal surface depends on the oxygen-containing groups on the surface. Furthermore, this adsorgtion was due to electrostatic forces and is ionic in nature. It was also reported that in the case of oxidized coals, the anion adsorption was probably insignificant compared to the hydrogen ion adsorption. The . authors suggested that weakly dissociating organic acids (succinic and adipic) were adsorbed on the surface of both run of the mine and oxidized coals by a mechanism which involved the interaction between the apolar part of the acid and the coal surface. This mechanism was referred to as a molecular mechanism. Highly dissociating organic acids (oxalic and malonic) were adsorbed on the surface by a mixed mechanism i.e. partly ionic and partly molecular.

The adsorption of n-hexanol and hexanoic acid from aqueous solution on the microcomponents of oxidized coal of type Zh was also reported (121). The observed increase in the amount of hexanoic acid adsorbed with increasing oxidation was attributed to the prevalence of an ionic mechanism. The main difference in the behavior of aliphatic alcohols and acids in aqueous solutions is that the latter are capable of dissociating and their adsorption is determined not only by their concentration of

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undissociated molecules but also by the concentration of ions. The adsorption of hexanol on unoxidized hydrophobic coal as well as on vitrinite and fusinite takes place with the alcohol oriented with the long axis of the carbon chain parallel to the plane of the adsorbent and the hydroxyl group projecting into the bulk of the solution. On oxidation of the coal, the interaction of the hydroxyl group of the algohol with the coal surface increases and adsorption takes place through the functional groups (122).

Recently, Fuerstenau and Pradip (74) studied the adsorption of phenol and three commonly used frothers, α -terpineol, methylisobutyl carbinol (4-methyl-2-pentanol, MIBC), and o-cresol (2-hydroxy-toluene) on coal surfaces. These authors found that the rate of attaining adsorption equilibrium was unexpectedly slow, possibly due to pore diffusion. They also reported that the adsorption of these nonionic surface active agents on oxidized coal is reduced, because of the possible increase in the hydrophilicity of the oxidized coal. They concluded that adsorption occurred through hydrophobic interactions between the frother molecules and the coal surface. Surface areas of the coal , and free energies of adsorption were determined on the basis of Langmuir-type isotherms. Surface areas of 23.6 m²g⁻¹ and 34.1 m²g^{w1} based on phenol adsorption were reported for a run of the mine coal called Geneva Mine coal and HF-treated anthracite respectively. Free energies of adsorption estimated for α -terpineol, o-cresol and phenol

on Geneva Mine coal were -40.6, -34.3 and -33.4 kJ mol⁻¹.

Miller et al. (75) found that dextrin, а polysaccharide with a dextrose monomeric unit, adsorbs by hydrophobic interactions on the coal surface. It was also reported that demineralized coal exhibited an adsorption density twice the adsorption density of natural coal and that adsorption decreased with increased oxidation but was largely independent of pH. Free energies of adsorption, based on Langmuir-type plots, of about -23.0 kJ mol⁻¹ were also reported. On the other hand, Kosman and Rowell (123) proposed that the cationic surfactant Atlas G-271 (N-soya-N-ethylmorpholinium ethosulfate) was adsorbed on the coal surface not only from hydrocarbon medium but also from water as an ion-pair unit with the polar head group oriented toward electron donating sites on the coal matrix and the hydrocarbon tail extending outwards to the solution phase.

The adsorption of dodecylpyridinium chloride (DPC), sodium dodecylbenzenesulfonate (ABS) and a nonionic polyoxyethylene nonylphenyl ether (NP-7.5) surfactants on Japanese coals was also studied in relation to the corresponding change of zeta potential (69). The results indicated that the adsorption of these surfactants was in the order

DPC > NP-7.5 > ABS The zeta potential of each coal increased positively with increasing concentration of DPC, while it remained constant

with increasing concentration of NP-7.5 and increased negatively with increased adsorption of ABS. In the case of the adsorption of the cationic surfactant, DPC, the results appear to indicate that the adsorption of DPC on these coals increases rapidly with the concentration of the surfactant and that an adsorption plateau was reached above the CMC. The two mechanisms proposed for the adsorption of DPC on the coal surface were (1) at low surfactant concentration, the positively charged head group of the DPC molecule is oriented towards the negatively charged sites on the coal and (2) at higher surfactant concentration, the DPC molecules are adsorbed on the nonpolar surface of the coal with the polar head group extending outward in the aqueous phase. In this study no mention was made of the pH of the system except that all but one of the coals used were found to be negatively charged in conductivity water.

In conclusion, several factors must be considered in elucidating the nature of the interaction of surfactants with a coal surface. The nature of the surfactant molecules themselves and the medium from which they adsorb onto the coal surface are important. Equally, the very nature of the coal surface, strongly influenced by its history is equally important. Since coals are usually porous, the variation of pore size and the adsorptionkinetics must also be taken into consideration when studying the interactions of molecules of various sizes

with coal.

IV.3 Results and discussion *

IV.3.1 Characterization of coal sample

The coal sample was characterized by both proximate and ultimate analyses (section III.2). The results are given in Table IV.1, where it should be noted that the percent moisture is as determined after grinding and evacuation. The ash content of the coal is rather low. The reason for using such a coal was, as Fuerstenau (74) suggested, to avoid complications arising from the presence of entirely different surfaces i.e. coal and mineral. The isoelectric point of this coal was at pH 5.3 in 10^{-4} m NaCl (Chapter V).

IV.3.2 On the use of spectrophotometry in the study of surfactant adsorption in suspensions

A number of experimental techniques have been used to determine quantatively the concentration of Surface active agents (39,61). These include titrimetry, gravimetry, surface tension measurements and direct spectrophotometry (section III.4). The use of direct spectrophotometry in determining free surfactant concentrations depends on the sensitivity of the maximum absorption peak to change in the solution concentration. Figures IV.1, IV.2 and IV.3 show the ultraviolet maximum absorption peaks of HPB, DPC and TPB respectively. No shift in the peak of maximum, absorption was observed in the calibration curve nor in the



Figure IV.1. Variation in absorbance with wavelength for HPB (1) calibration curve, conc.=5.82 x 10^{-5} m, pH=2.3, (2) calibration curve, conc.=1.25 x 10^{-4} m, pH=4.9, (3) calibration curve, conc.=1.75 x 10^{-4} m, pH=10.5. 1 = 1cm cell.



Figure IV.2. Variation in absorbance with wavelength for DPC. (1) coal-water supernatant, (2) coal-DPC supernatant, (3) calibration curve, $c=1.424 \times 10^{-4} m$. pH=4.5. l=1 cm cell.



Figure IV.3. Variation in absorbance with wavelength for TPB. (1) coal-water.supernatant, (2) coal-TPB supernatant, (3) calibration curve, c=1.620 x 10^{-4} m. pH=7.1. l=lcm cell.





coal-supernatant at the various pHs studied for these alkylpyridinium surfactants. The calibration curves were found to be very reproducible and linear over the range of concentrations studied. However, the coal-supernatant blank solution does show an absorbance at each of the wavelengths of maximum absorption studied (Figures IV.2 and IV.3). This is perhaps due to some water soluble compounds from the coal surface. Similar results were reported by Nogly (125) and by Kelebek (126). As a result the adsorption data obtained from direct spectrophotometry were corrected.

IV.3.3 On the use of surfactant electrode in the study of surfactant adsorption in suspensions

Experimental techniques such as spectrophotometry, titrimetry and gravimetry, that have been used to determine free concentration of ionic surfactants, become increasingly more difficult at lower concentrations in particular in the case of coal- or other suspensions such as studied here. Use of surfactant selective electrodes in adsorption studies has the advantage of very good sensitivity and reproducibility, small volume and tolerance of the presence of large excess of electrolytes and of solid particles. Figure IV.4 shows the response of the DTA⁺ electrode without and with excess sodium chloride. The cationic surfactant selective electrode shows Nernstian response from the critical micelle formation concentration, (CMC) down to about $2x10^{-5}$ m even in the presence of a Figure IV.4. Response of the DTA⁺ electrode to change in DTAB concentrations (a) \bigcirc salt free and (b) \triangle in 0.05 m NaCl. c=moles/kg H₂O.



large excess of sodium chloride (0.05 m inthe case presented). The excellent reproducibility of the potential allows us to use a plot of emf vs log c (c is the molal surfactant concentration) as calibration curve.

Figures IV.5, IV.6 and IV.7 show the observed potentiometric curves for the various solution mixtures under investigation and their deviation from the calibration curve. From these data, adsorption isotherms, as shown for example in Figure IV.13, can be constructed. The measurement is relatively easy in that the electrode can be inserted directly into the colloidal suspension without prior removal of turbidity by centrifugation (106). In the case of titration and spectrophotometry, "turbidity removal is essential prior to analysis, but even then the . measurement may still be subject to ambiguity. Surface tension measurements are sensitive to contamination by other surface active materials. However; it should be pointed out that the use of the surfactant membrane ion selective electrode is restricted by the pH of the coal suspension in that the response time of the electrode is very long even at high surfactant concentrations when the pH > 10 or < 4. The surfactant ion membrane electrode works very well between pH 4 and 10 and can be used e.g. in flotation cells to follow the changes in concentrations of these surfactants during flotation. Accuracies and reproducibilities are easily sufficient to allow for comparative studies between different dals, different

Figure IV.5. Response of the DTA⁺ electrode to the change in DTAB concentration in coal fine centrifugates. pH=7.8. c=moles/kg H₂O. • - calibration curve. c is the amount of DTA⁺ on the coal. c_D^f is the corresponding equilibrium molal concentration. c_D^i is the initial molal concentration.

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Figure IV.7. Response of the TP⁺ electrode to the change in TPB concentration in coal fine centrifugates. pH=4.1. $c=moles/kg H_2O$. $\bullet -$ calibration curve.



degrees of oxidation of the coal, influence of salinity and, to a certain extent, influence of pH.

IV.3.4 UV spectrophotometry vs emf measurements

Figures IV.8 and IV.9 illustrate a comparison of the spectrophotometric and the potentiometric methods to determine the adsorption of the surfactant, in this instance DPC and TPB respectively, on coal at its natural pH i.e. the pH of coal fines directly suspended in 10^{-4} m NaCl (pH = 4.3 to 4.7, z = +20mV to +1lmv), and at a pH where the coal is negatively charged. The results indicate that within the experimental error associated with each method of measurement, both methods produce similar results. Again, the use of the surfactant ion membrane was preferred when conditions, for instance pH of the suspension, permitted.

IV.3.5 Time dependence of surfactant adsorption on coal

In section IV.3.2, it was mentioned that the data obtained by direct spectrophotometry had to be corrected because the coal-water supernatant displayed an absorbance which might, for instance, be due to water soluble organics present in the coal used. Figure IV.10 shows how the coalwater supernatant absorbance depends on the contact time. The absorbance of the supernatant solution of a coal water mixture was measured at 259.1, 269.9 and 278 nm respectively. The absorbance was found to be constant and was used to correct for the final concentration of all

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Figure IV.8. Comparison of the spectrophotometric and the potentiometric methods for the adsorption of DPC on coal. $\nabla_1 \bigcirc$ pH=4.6 and 4.5; \triangle , \square pH=7.6 and 7.9. \bigcirc , \square potentiometry, $\nabla_2 \land$ spectrophotometry. c=moles/kg H₂O.

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Figure IV.9. Comparison of the spectrophotometric and the potentiometric methods for the adsorption of TPB on coal. $\bigcirc, \bigtriangledown$ pH=4.3 and 4.1; \triangle, \square pH=6.7 and 7.1. $\triangle, \bigtriangledown$ potentiometry \bigcirc, \square spectrophotometry. c=moles/kg H₂O.



* **4**1 'Figure IV.10. UV. absorbance of pure water in contact with coal fines vs. contact time. \Box, λ =259.1 nm, O, 8 λ =269.9 nm, \triangle , λ =278.0 nm. đ l 95



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species determined by spectrophotometry.

The adsorption kinetics of phenol, Triton X-100 and DTAB are shown in Figure IV.11 while those for DPC, TPB and. HPB are shown in Figure IV.12. In all cases, except for phenol, adsorption equilibrium is essentially reached within the equilibration time of 23 hours used in our adsorption experiments. In the case of phenol, adsorption. is found to increase even after up to 300 hours of contact Similar results have been 'reported by Fuerstenau and time. Pradip (74). This may be indicative of the porous nature of the coal, with the phenol molecules being adsorbed into small pores of the coal which cannot be reached by the larger hydrophobic chain of DTAB, DPC, TPB and HPB nor by the larger alkylphenolpolyethylene oxide molecules of Triton X-100. As Figure IV.11 illustrates, the amount of Triton X-100 adsorbed, even on a molar basis, is actually significantly larger than for phenol, at least for times less than 100 hours while the adsorption of HPB is considerably higher than that of the C_{12} surfactant, DPC and the C₁₄ surfactant, TPB. On the other hand, the adsorption of Triton X-100 and HPB appears to be similar. Another possible explanation for the higher HPB and Triton X-100 adsorption, at least at short contact times, relative to the other surface active agents might be that the small pores of the coal surface are not wetted with water, phenol, and the C_{12} and C_{14} surfactants, or only very slowly, but are wetted rapidly with HPB and Triton X-100.





Figure IV.12. Time dependence of the adsorption of surfactant on coal at the natural pH. (1) \Box DPC, pH=4.8 \pm 0.1, (2) \triangle TPB, pH=4.2 \pm 0.1, (3) \bigcirc HPB, pH=4.7 \pm 0.1.



cFrom this study, it can be concluded that although a pore mechanism might be responsible for the initial increase in adsorption (for times shorter than maybe 10 hours), it is also possible that the ability of the surfactant to "wet" the coal surface and indeed the pores might also contribute to the increase in adsorption of the particular surfactant. The greater adsorption of HPB on coal can, also be attributed to the longer hydrophobic chainlength compared with either DPC or TPB perhaps suggesting that the important adsorption mechanism at this pH (where the coal is positively charged) is a hydrophobic' interaction of the surfactant and the coal surface. In the case of Triton X-100, we might conclude that either phenol finds fewer specific adsorption sites than the amphiphilic Triton X-100 molecules, that Triton X-100 "wets" the coal surface and the pores more rapidly than phenol, or that Triton X-100 molecules undergo "end-on" and/or multilayer adsorption even at rather low solution concentrations, leading to relatively high amphiphile adsorption as compared to phenol. Obviously, surface area determinations based on phenol adsorption will depend on coptact time and, if taken after less than 48 hours, may not include the area. of the finest pores.

IV.3.6 Adsorption of simple organic molecules

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Adsorption otherms for phenol and p-nitrophenol, at the natural pH of the coal suspension, and taken after 23 hours of contact time, are presented along with their

respective linearized Langmuir plots in Figures IV.13 In the case of phenol adsorption on carbon, an IV.16. adsorption mechanism, involving both hydrophobic interactions and m-bonding interactions between the phenol π -electrons and the carbon surface has been suggested (112,113,117,124). It has also been argued that at high solute concentrations, these molecules tend to be. reoriented to an "end-on" position, giving rise to a twostep adsorption isotherm (124,127). The phenol adsorption isotherm in Figure IV.13 levels off at about (3.95 ± 0.40) $x = 10^{-6}$ moles phenol adsorbed per g coal with no indication of a second adsorption step within the concentration range studied. If we assume that the phenol molecule is positioned flat on the active coal surface, and using an area for the phenol molecule of 0.41 nm^2 (74), we find the active surface area of coal covered by phenol to be (0.98 ± 0.10) $m^2 q^{-1}$.

Although this value is quite typical for various coals, (69, 75, 120), it is obvious from the discussion in the previous section that surface areas determined with different adaptates may give entirely different results. For example since coals are normally porous, the surface available for adsorption may not be the same as that by BET method when either nitrogen or carbon dioxide is used as adsorbate. Furthermore, it should be mentioned that the choice of slope of the linearized Langmuir isotherm in which some non-linearity is evident is also important in

Figure IV.13. Adsorption of phenol on coal at natural $pH=4.5 \pm 0.1$. $c=mole/kgH_2O$.



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Figure IV.14. Linearized Langmuir isotherm for the adsorption of phenol (pH=4.5 \pm 0.1). c= moles/kg H₂O. c/x = g coal/kg H₂O.



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Figure IV.16. Linearized Langmuir isotherm for the adsorption of p-nitrophenol (pH=4.5 \pm 0.1). c=moles/kgH₂O. c/x = g coal/kg H₂O.

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surface areas determinations (section II.3). In the surface areas and free energies of adsorption calculations, we have taken the low concentration or higher slope of the linearized Langmuir isotherm in each case. In a few cases (phenol, p-nitrophenol, Triton X-100), the low concentration slope happened to be about equal to the total slope.

Fuerstenau (74) suggested that the well-characterized case of phenol adsorption may be used to assess the surface area available on coal for adsorption from solution. On the other hand, p-nitrophenol (Figure IV.15) has a maximum adsorption almost three times higher than phenol with indications of a two-step adsorption mechanism. If we can assume that this is caused by multilayer adsorption, this appears to commence at a free p-nitrophenol concentration of about 5.4 \times 10⁻⁵ m, and at a surface coverage of about 6 \times 10⁻⁶ moles/g coal.

IV.3.7 Adsorption of surfactants

The adsorption of the nonionic surfactant, Triton X-100, is shown in Figure IV.17 and the corresponding linearized Langmuir plot in Figure IV.18. Triton X-100 shows about the same maximum adsorption density capacity as p-nitrophenol, but the adsorption plateau is reached only at higher solution concentrations. The adsorption isotherms of the cationic surfactants, dodecyltrimethylammonium bromide (DTAB), dodecylpyridinium chloride (DPC), tetradecylpyridinium bromide (TPB),

Figure IV.17. Adsorption of Triton X-100 on coal at natural

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pH=4.5 \pm 0.1. c=mole/kgH₂O.

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Figure IV.18. Linearized Langmuir isotherm for the adsorption of Triton X-100 (pH=4.5 \pm 0.1). c=moles/kgH₂O. c/x = g coal/kg H₂O.





hexadecylpyridinium bromide (HPB), at various suspension pH values and their linearized Langmuir isotherms (at the natural pH) are shown in Figures IV.19 - IV.26. In. general, adsorption is found to be strongly pH dependent, with higher suspension pH leading to higher surfactant adsorption. This may be indicative of a surface charge effect on the adsorption of the cationic amphiphile, or it may simply mean that additional anionic sites become available on the coal surface as the pH is increased. The adsorption isotherms do not show the three distinct regions observed by Gala et al. (71) for the adsorption of DPC on '-32 mesh Pittsburg seam coal, nor do they exhibit the apparently increasing adsorption evident from the data of Esumi et al. (69), also for DPC but with points at very high concentrations.

Figure IV.27 illustrates a comparison of the adsorption of DTAB, DPC, TPB, HPB on coal at approximately constant pH. The adsorption at any given surfactant concentration increases as the chainlength of the hydrocarbon tail increases i.e.

 $C_{16}^{P^+} >> C_{14}^{P^+} > C_{12}^{P^+} > C_{12}(N)^+(CH_3)_3$

Although the pHs are somewhat different leading to different zeta potentials, i.e. $\zeta = -34$ mV at pH 7.1 and $\zeta = -52$ mV at pH 8.6, the increase in adsorption is probably due not only to the increase in negative sites on the coal but to some hydrophobic interaction of the

Figure IV.19. Adsorption of DTAB on coal at different pH. O $pH=4.7 \pm 0.1^{\circ}$ (natural pH), $\triangle pH=7.8 \pm 0.1$. c=moles/kgH₂O.

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Figure IV.20. Linearized Langmuir isotherm for the adsorption of DTAB at natural $pH=4.7 \pm 0.1$. c=moles/kg H₂O. c/x = g coal/kg H₂O.







Figure IV.22. Linearized Langmuir isotherm for the adsorption of DPC at natural pH=4.5 \pm 0.1. c=moles/kg H₂O. c/x = g coal/kg H₂O.

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Figure IV.23. Adsorption of TPB on coal at different pH. \bigcirc pH=4.3 ± 0.1 (natural pH), \triangle pH=7.1 ± 0.1, \square pH=9.1 ± 0.1. c=moles/kg H₂O.



Figure IV.24. Linearized Langmuir isotherm for the adsorption of TPB at natural pH=4.3 \pm 0.1. c=moles/kg H₂O. c/x = g coal/kg H₂O.

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Figure IV.25. Adsorption of HPB on coal at different pH.

 \bigcirc pH=4.8 ± 0.1, △ pH=6.4 0.1, □ pH=8.6 ± 0.1, \bigtriangledown pH=10.0 ±

0.1. c=moles/kg H₂O.

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adsorption of HPB at natural pH=4.8 \pm 0.1. c=moles/kg H₂O.


Figure IV.27. Comparison of the adsorption of various surfactants on coal. \bigcirc DTAB, pH=7.8; \triangle DPC, pH=7.9; \square TPB, pH=7.1 and \bigtriangledown HPB, pH=8.6. c=moles/kg H₂O.



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surfactant tail and the coal surface, this interaction being stronger as the chainlength increases. Also the adsorption of DPC is somewhat greater than that of DTAB. Since both surfactants have a C_{12} alkyl chain, one can interpret this increase in adsorption in terms of the aromatic ring playing some part in the adsorption mechanism of the dodecylpyridinium cation relative, to the dodecyltrimethylammonium entity. Again this is possible since the π -electrons of the aromatic ring can interact, with the surface of the coal (61,66,74,112,124).

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The free energies of adsorption of each surface active agent can be calculated from the linearized Langmuir plot if we assume the isotherms to be Langmuirian type. These are shown in Table IV.2. The errors in ΔG_{ads} are obtained from the standard deviations in the intercept of the linearized Langmuir isotherm. It is of some importance to include such error estimates in ΔG_{ads} values, in order to prevent unrealistically detailed discussions of small differences in ΔG_{ads} sometimes found in the literature. Thus the free energies of adsorption of phenol and pnitrophenol are essentially equal. Comparing the $\[A]$ G_{ads} values for the cationic surfactants, we find that the free energies of adsorption of DPC and TPB are essentially the same, that of HPB marginally lower while that for DTAB slightly higher. The ΔG_{ads} of Triton X-100 is the lowest and this lower free energy adsorption might be explained by an "end-on" mechanism.

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Surface areas and free energies of adsorption on coal by different adsorbates¹.

Adsorbate	Surface area (m ² g ⁻¹)	Area per molecule adsorbed using phenol as referenc (nm ²)	- ΔG (kJ mol-1) e
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phenol	0.98 ± 0.2	0.41	28.7 ± 2.2
p-nitrophenol	<u> </u>	0.25 ± 0.03	28.1 ± 2.2
Triton X-100	-	0.12 ± 0.02	23.8 ± 1.6
DTAB (pH 4.7)	-	0.42 ± 0.09	35.7 ± 2.5
DPC (pH 4.5)	ير ، 	0.37 ± 0.08	34.0 ± 1.0
TPB (pH 4.3)	. –	0.26 ± 0.01	32.0 ± 1.0
HPB (pH 4.8)	-	0.17 ± 0.01	30.1 ± 2.2

¹error estimates are from the standard deviations of the linearized Langmuir isotherm.

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If it assumed that adsorption of the various surface active agents occurs at the same sites as phenol adsorption, then the adsorption area per molecule of each surface active agent using phenol surface areas as a reference can be calculated from the respective linearized Langmuir isotherm. Such areas are presented in Table IV.2. Again the error estimates for the surface areas are obtained from the standard deviations in the slope of the linearized Langmuir plot. The surface area per molecule of Triton X-100 and HPB appears to be similar and lower than the other surface areas. In the case of Triton X-100, the sharply lower value may be caused by additional surface sites specific to the alkylphenol amphiphile, by the ability of this surfactant as well as HPB to "wet" the pores more rapidly than the other surfactants, by multilayer adsorption, or by an "end-on" adsorption mechanism where only a small part of this molecule is in contact with the coal surface.

The possibility of multilayer adsorption is certainly not apparent from the relatively smooth Langmuirian adsorption isotherm (Figure IV.17). If the ethylene oxide chains are adsorbing, then the coal surface becomes more hydrophobic with increasing adsorption of Triton X-100, until multilayer adsorption occurs. On the other hand, the "end-on" mechanism might explain the slightly lower free energy of adsorption and the fact that Triton X-100 is an excellent wetting agent (128) for coal even at low

concentrations, further indicates that the hydrophilic part of the molecule is indeed in the aqueous phase.

Finally, we observe a definite levelling off of the surfactant-coal adsorption isotherms at the natural pH unlike the results of Esumi and others (69-71). Esumi et al. found very low areas covered per DPC molecule, typically in the range 0.01 - 0.07 nm², at least at the higher surfactant equilibrium concentrations. The "standard" area used in these calculations was based on nitrogen adsorption. These very low areas probably indicate multilayer adsorption at the very high equilibrium concentrations of DPC studied.

CHAPTER V

ELECTROPHORESIS OF COAL PARTICLES

V.1 Introduction

In Chapter III, we discussed the interpretation of the zeta potential and the relation between electrokinetic potentials and flow behavior of colloidal systems has been examined. This chapter examines the applications of the zeta potential in coal and mineral science, particularly the extent to which ζ -potential can be used as a tool to study features of charge distribution at the coal interface in the presence of a simple salt and several surfactants. A model which has been applied to electrokinetic data on adsorption of surfactants at the solid-liquid interface will be examined and compared to the coal-surfactant systems studied.

A large number of authors (e.g. 30,34,71,75,129-140) have described electrokinetic properties (zeta potentials derived from electrophoresis or streaming potential) for a variety of particles and adsorbates, for example simple inorganic oxides, silver halide sols, glass, clays and simple inorganic ions to more complex organic adsorbates. As a result, no attempt is made to review the literature exhaustively and only the research relevant to the present study will be discussed. In spite of difficulties inherent in the theory relating measured quantities to zeta

potentials, it is still possible to establish a useful correlation between a desirable but yet difficult to measure parameter, for instance flow behavior of colloidal systems, and the electrokinetic potential of the system (129). Typically, it has long been recognized that the zeta potential is a good index in assessing the stability of a colloidal sol (43,130-133). The efficiency and control of flocculation or coagulation can be achieved by routine zeta potential measurements (133).

The general emphasis of this chapter will therefore be on the use of electrokinetic data in understanding the nature of the interaction of the surfactant with the coal surface. As Hunter (46) suggests, emphasis will be placed on the variation of electrokinetic quantities with various variables rather than on what is meant by a single electrokinetic potential measurement.

V.2 Point of zero charge

The ionic species that exert a fundamental control on the surface charge and the potential of the dispersed phase are called the potential determining ions (pdi). The ionic species that control in general the extension of the double layer out into the solution but are not involved in any specific interaction with the surface are referred to as indifferent electrolyte ions. The particular bulk concentration of the potential determining ions for which the surface charge is zero is termed the point of zero . charge (pzc) and is determined by a direct measurement of the surface charge as a function of the pdi concentration. Since other ionic or polar species may absorb on a surface, the surface charge effective in electrokinetic experiments may not be zero at the pzc. The point at which the pdi concentration has been adjusted to make the zeta potential zero is called the isoelectric point (iep). In the absence of specific adsorption of any ionic or polar species and of other source of charge, the pzc and iep are equal (134).

V.3 <u>Theory of ionic surfactant adsorption on mineral</u> <u>surfaces</u>

In recent years, understanding of the nature of the surfactant adsorption process has been greatly improved by the adsorption and electrokinetic studies of especially Ottewill, Fuerstenau, Healy, Somasundaran and others. **(43,46,132,135-139)**. Although surfactant adsorption studies on coal are relatively scarce, a wealth of information exists concerning their adsorption from water on various minerals such as oxides, and it is useful to compare our work with the results of such studies. The theoretical treatment of ionic surfactant adsorption on mineral surfaces essentially retraces the work of Ottewill (43,132) and Fuerstenau (135-139) and is generally based on an elaboration of the Gouy- Chapman-Stern-Grahame model of the double layer.

Briefly, the system is best exemplified by the treatment of the adsorption of longchain alkyammonium ions on quartz (137). At low concentrations, the surfactant

adsorbs in much the same way as any positive ion but at a certain critical concentration of surfactant there is a sudden change in the *r*-potential and a rapid increase in adsorption density which is attributed to "hemi-micelle" formation i.e. a two-dimensional association on the surface instead of the usual three-dimensional association to form micelles in bulk solution.

Grahame's treatment of the compact double layer (56,132,137) leads to the following expression for the adsorption of surfactant ions

 $\Gamma_{+} = 2rc \exp(-\Delta G^{O}_{ads}/RT)$

where

 $\Delta G^{O}_{ads} = z \varepsilon \psi_{\delta} + h \phi + \phi_{HG} \qquad (V.2)$

(v.1)

 $z_{\epsilon}\psi_{\delta}$ represents the coulombic interaction with the surface charge in the double layer, $\phi_{\rm HG}$ is the interaction of the head group with the surface, ϕ measures the interaction of each of the n CH₂ groups between adjacent chains of the adsorbed surfactant molecules, r is the radius of the adsorbing ion and c is the surfactant concentration. At the point of zeta potential reversal (pzr) i.e. when the surfactant adsorption has reduced the ζ -potential to zero, ψ_{δ} is set to zero and equation (V.1) becomes

 $\ln c_0 = (\ln r_{+,0} - \ln 2r + \phi_{HG}/kT) + n\phi/kT$ (V.3)

A plot of $\ln c_0$ (where c_0 is the surfactant concentration at the pzr) against chainlength, n, is linear with slope

equal to $-\phi/kT$.

The assumptions inherent in equation (V.3) include (i) the potential difference between the OHP and the shear plane is small compared to the total potential across the double layer, (ii) the term in parentheses in equation (V.3) is constant at the pzr.

V.4 eview of related studies

Few authors have studied the effect of electrolyte and surface active agents on coal surfaces electrokinetically. Klassen (140) studied the fixation of frothers on coal electrokinetically. He found that alcohols are actively adsorbed by coal, and to a much lesser extent by gangue minerals. The adsorption is greatest for alcohols with 6-8 Jowett (141) used zeta potential carbon atoms. measurements in work involving slime coating of coal by clay in flotation pulps. Zeta potential measurements for both the slimes and the coal were found to be negative in deionized water. Fushimi (142) used electrophoretic measurements in experiments on the flotation of coal. He found that the electrophoretic velocity of coal particles was inversely proportional to the ash content. Campbell and Sun (30,143,144) measured, using a streaming potential method, the zeta potential of Pittsburg bituminous coals and their lithotypes as well as that of an anthracite coal. They reported that H^+ and OH^- were the potential determining ions (pdi). The measured iep of the bituminous coals was in a pH range between 3.5 and 4.6 and for the

anthracite between pH 2.0 and 4.5. They also found that the iep for a specific lithotype of one particular coal seam was different from the iep of the same lithotype of another coal seam. They concluded that since the iep, and hence the hydrophobicity of the lithotypes, were pH controlled, then the flotation of the lithotypes using oily collectors would also be controlled by the pH.

Wen and Sun (145,146) investigated the electrokinetic behavior of oxidized Pittsburg coals, by microelectrophoresis, in the presence of various inorganic salts and dodecylamine. The iep reported for anthracite, LVbituminous, HVA-bituminous and lignite were respectively 5.0, 4.6, 4.5 and 2.3. The iep of the HVA-bituminous coal decreased as oxidation increased. Again, the H⁺ and OH⁻ ions were found to be potentially determining. Charge reversal of oxidized HVA-bituominous coal was observed in the presence of 10^{-4} M Fe³⁺ and Fe²⁺ ions and dodecylamine (1-amino-dodecane) respectively while Ca^{2+} , Mq^{2+} and Na^{+} ions had no effect on the zeta potential of this coal. Attempts to describe the role of surface forces in wet cleaning methods of fine coal have included maximum hydrophobicity of the coal surface relative to the attendant mineral matter, and it has been suggested that a criterion for hydrophobicity of coal is that it should have a point of zero charge (24,33,144-147). On the other hand, Jessop and Stretton (148) disagree with this view. They concluded from their study that the zero point of charge is not a

criterion for hydophobicity 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 a particular ion or surface active agent is adsorbed at the surface. Another hypothesis (149) argues that the contamination of the coal surface as well as oxidation might be responsible for its negative surface charge.

Fuerstenau, Somasundaran and others (34,135-139,150) have discussed interfacial processes in mineral/water . systems. They have correlated measurements that reflect conditions at the solid/liquid interface (adsorption density and zeta potential) with surface phenomena reflecting conditions at the said/liquid/air interface (contact angle). . Perhaps the best system representing this kind of reasoning is the adsorption of longchain alkylammonium $(C_{10}-C_{18})$ acetates on quartz studied by Somasundaran et al. (138). From adsorption isotherms and electrokinetic behavior of the mineral-surfactant system, they suggested that at low concentrations, the surfactant ions are adsorbed as individual counter ions, while at high solution concentrations interactions between the hydrocarbon chains of those ions adsorbed in the Stern layer cause increased adsorption. This surface aggregation process is called "hemi-micelle" formation. From the chainlength dependence of the charge reversal concentration, these authors calculate the surfactant-

surfactant hydrophobic interaction to be about 0.97 kT (2.4 kJ mol⁻¹) per CH_2 group. This is slightly less than the free energy of transfer of a CH_2 group from water to hydrocarbon medium, which is about 1.3 kT (43).

Nicol and Hunter (151) studied the adsorption of longchain trimethylammonium ions $(C_{10}-C_{14})$ on kaolinite and reported the value of 1.2 kT per CH_2 group for the surfactant-surfactant interaction. Similarly Rendall et al. (152) found that the adsorption on a nylon sol of a series of aliphatic sulfonates $(C_{10}-C_{16})$ increases by about kT per CH_2 group. Recently, Gala et al. (71) reported that the adsorption of the cationic surfactant dodecylpyridinium chloride, DPC, on coal followed a mechanism similar to the surfactant-quartz system studied by Somasundaran et al. (137).

V.5 <u>Results</u> and <u>discussion</u>

V.5.1 <u>Measurement of electrophoretic mobility by</u> microelectrophoresis

Traditional methods for measuring electrophoretic mobility have been tedious and slow. The transit time of a particle is measured over a fixed distance in the microscopic eyepiece. This is repeated again and again for different particles in order to compute a statistically significant mean mobility. Poor image contrast and difficulty of keeping track of the selected particle add to operator fatigue. The tendency, when timing individual particles, to pick out the big bright ones which may not be typical of the total population leads to operator bias in the reported results. The Carl Zeiss cytopherometer operates on such a principle. On the other hand, the Rank Brothers Mark II microelectrophoresis apparatus with the rotating prism measures the movement of a large number of particles at the same time. Modern instruments such as this one are designed to make zeta potential measurements quick, easy and accurate.

Figure V.1 illustrates the zeta potential as determined by both the Carl Zeiss cytopherometer, and the Rank Mark II apparatus using the flat cell, both under identical conditions (-200 mesh, 10^{-4} m NaCl). The results are identical within expected experimental error. Platinum electrodes were used in the Carl Zeiss cytopherometer while both platinum and palladium electrodes (153) were used in the Rank Mark II instrument. We found that the palladium electrode precharged with hydrogen (153) was more useful thanthe platinum electrodes especially at high electrolyte concentration as the use of palladium electrodes eliminates the problems of electrode polarization. The rotating prism method has an advantage over the one-particle measurement method in that a large number of particles are, in effect, observed at once and this gives a better distribution of the total particle population. However, there is a greater scatter in the data obtained by the Rank Mark II than with the Carl Zeiss. This is due to the fact that the rotating prism gives a better distribution of the particles whose

Figure V.1. Comparison of the zeta potential as determined by the Carl Zeiss cytopherometer (open symbols) and the Rank apparatus (flat cell) (closed symbols) of coal particles in surfactant suspensions. O, \blacksquare DTAB pH 4.5, 4.7; \bullet , \Box DPC pH 9.0, 9.2.


electrophoretic mobility is being measured and hence an average mobility perhaps closer to the actual particle mobility than the one-particle of the Carl Zeiss instrument. In other words the seemingly lower scatter shown for the data collected with the Carl Zeiss cytopherometer may in fact reflect a combination of restricted particle selection and operator bias. We also compared the electrophoretic mobility as determined from both the flat cell and the cylindrical cell of the Rank Mark II apparatus using the potassium chromium sulfate hydrosol, $KCr(SO_4)_2.12\dot{H}_2O_7$, employed by Hepler (154), as well as coal particles. The electrophoretic mobility for $KCr(SO_4)_{2}$, 12H₂O was found to be 1.41 ± 0.03 µms. $1/Vcm^{-1}$ (flat cell) and 1.44 ± 0.10 $\mu m s^{-1}/Vcm^{-1}$ (cylindrical cell). Hepler et al. (154) described a velocity-depth profile method used to calculate electrophoretic mobilities of colloidal particles. These authors state that normal microscopic electrophoresis methods using only measurements at the plane of zero osmotic flow are known to be poorly reproducible. Thev reported, from velocity-depth profile measurements; a value of 1.64 \pm 0.12 µms⁻¹/Vcm⁻¹ for potassium chromium sulfate hydrosol, $KCr(SO_A)_2.12H_2O$. Our results compare extremely well with another literature value of 1.42 μ ms⁻¹/vcm⁻¹ (155) and moderately well with Hepler's result. • It should be mentioned that the velocity-depth profile method requires several measurements to obtain just

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electrophoretic mobility and hence can be more time consuming than even the one-particle measurement at the stationary plane. We found that the electrophoretic mobility of coal particles determined using the cylindrical cell was systematically about 5-10 per cent higher than when the flat cell was used. It should be noted that part of this error may be caused by the optical correction necessary with the cylindrical cell but not with the flat cell, a correction which may be in error if the thickness of the glass is not accurately known. Furthermore, location of the stationary plane is more critical in the cylindrical cell. Because of the fairly good agreement between the data obtained with the flat cells in both the Carl Zeiss and the Rank Mark II instruments for the coal particle electrophoretic mobility measurements, and the good correspondence for the potassium chromium sulfate hydrosol data obtained in these cells with literature values, we have used the flat cell of the Rank Mark II instrument for most of our investigations.

V.5.2 <u>Electrophoresis</u>

V.5.2.1 The effect of electrolyte on the electrokinetic potential of coal

Figure V.2 shows the zeta potential of the coal as a function of pH in the presence of varying concentrations of NaCl solutions. The isoelectric point (iep) of the coal in 10^{-4} m NaCl was at pH 5.2. There is a small acidic shift of the iep as the concentration of the electrolyte increases (Figure V.2, insert (a)). At a given pH, the

Figure V.2. Variation of zeta potential with pH at various salt (NaCl) concentrations. $\triangle 1 \times 10^{-4}$ m NaCl (iep 5.2); $\bigcirc 0.017$ m NaCl (0.1 %) (iep 4.6); $\square 0.034$ m NaCl (0.2 %) (iep 4.1); $\bigtriangledown 0.68$ m NaCl (0.4 %) (iep 3.8). Insert: iep vs. % NaCl; arrow: % NaCl of CBDC washing plant process water.



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absolute value of the zeta potential decreases with increasing electrolyte concentration. This is due to the compression of the electric double layer around the coal particle. The cross-over point for all four electrokinetic isotherms is at pH 6 when ζ is about -10 mV. This isperhaps indicative of some Cl- adsorption on the coat surface. Similar results were observed in the detailed electrokinetic studies of Angle and Hamza (156). Although the results suggest some Cl⁻ adsorption, i.e. NaCl may not be an indifferent electrolyte (section V.2), the dramatic effect that the pH exerts on the ζ-potential (and, by inference, the surface charge) indicates that H⁺ and OH⁻ are potential determining.ions in this system and that perhaps the H⁺ and OH⁻ are much more important than the Cl⁻ ions. Campbell and Sun (30) and Wen and Sun (145) likewise reported that H⁺ and OH⁻ ions were potential determining for several Pittsburg coals but NaCl was an indifferent electrolyte in those coal systems. The coal used in the present study is positively charged ($\zeta = \pm 10 \text{ mV}$) in deionized distilled water in contrast to the coal used in the studies of Wen and Sun (145) and the coals used by Esumi et al. (69).

V.5.2.2 The effect of surfactant on the electrokinetic potential of coal

The effect of surfactant adsorption on the electrokinetic potential of -200 mesh coal is shown in Figures V.3 - V.7. Figure V.3 shows that the zeta



Figure V.3. Effect of Triton X-100 on the zeta potential of coal at pH 4.7 \pm 0.1.



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Figure V.4. Effect of DTAB on the zeta potential of coal. \triangle pH 3.1 ± 0.1, \bigcirc pH 4.7 ± 0.1, \square pH 7.0 ± 0.1, \bigtriangledown pH 8.6 ± 0.1. NaCl concentration 1 x 10⁻⁴.



Figure V.5. Effect of DPC on the zeta potential of coal. \bigtriangledown pH 2.7 ± 0.1, \bigcirc pH 4.6 ± 0.1, \triangle pH 7.0 ± 0.1, \square pH \clubsuit .







161 . Figure V.6. Effect of TPB on the zeta potential of coal. ∇ pH 2.7 ± 0.1, O pH 4.5 ± 0.1, \triangle pH 6.8 ± 0.1, \square pH 8.2 ± 0.1. NaCl concentration 1 x 10⁻⁴.



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Figure V.7. Effect of HPB on the zeta potential of coal. \bigtriangledown pH 2.5 ± 0.1, \bigcirc pH 4.5 ± 0.1, \triangle pH 6.8 ± 0.1, \square pH 9.8 ± 0.1. NaCl concentration 1 x 10⁻⁴.

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potential is virtually unchanged by the addition of Triton X-100. This must mean that the shear plane is not noticeably changed by the adsorption of this non-ionic In a study of the stability of carbon súrfactant. suspensions, Kratochvil and Matijevic (157) reported that the point of zero charge (pzc) of all carbons studied shifted towards lower pH values with increasing concentration of Triton X-100. The electrokinetic mobilities are hardly affected by the addition of Triton X-100 at high pH values. However the carbon particles become less positive in the acidic range as the added surfactant concentration increases. Since it was also found that the adsorption of Triton X-100 was not pH dependent, they concluded that, in acidic solutions, the surfactant is adsorbed on the carbon surface in a "collapsed" configuration and consequently the shear of plane would be nearer to the particle surface in acidic suspensions. They claimed that this configuration would result from less hydration, presumably implying that the potential determining H^+ or H_2O^+ ions are displaced from the surface by the "collapsed", non-hydrated surfactant chain. In the coal-Triton X-100 system, the constancy in the zeta potential might suggest the adsorbed surfactant is indeed present in a "collapsed" configuration but without displacing plane of shear, or without displacing potential determining ions. Another possibly more simple explanation is that the Triton X-100 molecule is adsorbed mainly on the'

inner surfaces of the coal and as such does not influence the surface of shear.

On the other hand, the adsorption of the cationic' surfactants, DTA⁺, DP⁺, TP⁺ and HP⁺, strongly alters the electrokinetic potential of the coal. In general, when the coal is initially negatively charged (pH > iep), cationic surfactant adsorption causes charge reversal. However, for solution pH below the iep, the surface charge still increases upon surfactant adsorption, in spite of the fact that the surface charge is already positively charged. These observations seem to indicate that the adsorption of the cationic surfactants occurs through a combination of electrostatic and hydrophobic binding. The initial slopes of the electrokinetic isotherms for DPC, TPB and HPB are rather sharp and similar in contrast to the slope for DTAB. This is usually an indication of a highly favourable adsorption process and suggests that the adsorption of DP⁺, TP⁺ and HP⁺ is more favourable than that of DTA⁺. This is also shown in the adsorption isotherms of these surfactants on coal (Figure IV.27).

In view of an interpretation in terms of the adsorption mechanism, it is of particular interest to compare the chainlength dependence of these electrokinetic isotherms and the corresponding adsorption isotherms with the electrokinetic isotherms for surfactant adsorption on oxide mineral surfaces, reported by Somasundaran et al. (136-139,150). The theory of ionic surfactant adsorption

has been discussed in section V.3. From Figures V.4 and V.5, we find that charge reversal occurs at a free surfactant concentration of 6×10^{-5} m for DTAB at pH 7.0 and at 2.2 $\times 10^{-5}$ m for DPC at the same pH. Similarly, $\zeta = 0$ at 7.3 $\times 10^{-5}$ m for DTAB at pH 8.6 and at 3.3 $\times 10^{-5}$ m for DPC at pH 9.2. Charge reversal of the coal particle occurs at a higher surfactant concentration for DTAB than for DPC at a fixed pH. This is probably due to the added surface interactions of the pyridine ring of DPC with the coal. Similar results were reported on the behavior of silver iodide sols in the presence of the same cationic surface active agents by Ottewill (42,132,158).

Somasundaran et al. (137-139) found that the charge reversal for alkylammonium ions on quartz varies from about 2.2 x 10^{-3} M for C_{12} to about 6.6 x 10^{-5} M for C_{16} . When we consider Figures V.5 - V.10, we note a very different behavior for the surface charge reversal of coal due to alkylpyridinium cation adsorption. For example, in Figure, V.8 the surfactant concentration at zero charge ($\xi = 0$), sczc, determined from interpolations of the data in Figures V.4 - V.7, is found to be practically independent of the alkyl chainlength at a given pH, and equals about 8 x 10^{-6} m at pH 7, at which pH the zeta potential of the coal itself is about -30 mV. However, the sczc (surfactant concentration at zero charge) seems to be dependent on the added interaction of the pyridine ring of the alkylpyridinium surfactants since, for example, at pH 7 the
Figure V.8. Surfactant concentration at zero charge, sczc, at various pH. \bigtriangledown DTAB, \bigcirc DPC, \bigtriangleup TPB, \Box HPB.

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Figure V.9. Zeta potential at various pH of surfactant solution concentrations of 1 x 10^{-5} m (open symbols) and 4 x 10^{-5} m (closed symbols). ∇, ∇ DTAB; O, \bullet DPC; Δ, \blacktriangle TPB; \Box, \blacksquare HPB.



Figure V.10. Adsorption of surfactant on 'coal (moles/g coal), n_{zc} , at zero charge as a function of pH. O DPC, \triangle TPB, \Box HPB.



sczc is about 2.8 x 10^{-5} m for DTAB while, as previously mentioned, it is about 8 x 10^{-6} m for all the alkylpyridinium surfactants.

Figure V.9 shows that at a given pH and equilibrium surfactant concentration, the zeta potential varies regularly with pH and is practically independent of the surfactant chainlength. Yet, the actual adsorption density at the iep, n_{zc}, increases with increasing chainlength, as can be seen in Figure V.10. n_{zc} is calculated from the adsorption isotherms shown in.Figures IV.21, IV.23, and IV.25. Typically, again at pH 7, n_{zc} equals 2 x 10⁻⁶ mole/ g coal for DPC, 4×10^{-6} mole/ g coal for TPB and 8×10^{-6} mole/ g coal for HPB. According to Somasundaran et al. (137), a plot of in sczc vs. n (equation V.3) should determine the interaction of each CH₂ group between the adsorbed surfactants. In this -200 mesh coal-surfactant system, there is no such correlation between the chainlength and the concentration of the surfactant at zero zeta potential. As previously mentioned, the sczc of the alkylpyridinium surfactants seem to be independent of alkyl chainlength, for instance at pH 7 the sczc is about 8 x 10^{-6} m. The reproducibility of the sczc at these low surfactant concentrations is rather poor. Nevertheless,** the important point is that when the sczc for a C_{16} . surfactant is around 10^{-5} m, that for a C₁₂ surfactant should be around 10^{-3} m in accordance with the theory of Somasundaran et al. (137) and this is certainly not the

'case in this coal-surfactant system studied.

Osseo-Asare et al. (159) in a study of the electrokinetics of silver iodide sols in various longchain sulfonates, obtained a value of 0.50 kT for the interaction per CH2 and suggested that perhaps this low value was due to the surfactant molecules lying flat on the surface of the silver iodide at least near the iep. This might be the case in the coal-surfactant system or it might be that as the surfactant concentration increases, there is a displacement of the surface of shear and hence the measured zeta potential is not at the same distance from the surface. It should be noted that Mishra et al. (160) also did not observe "hemi-micelle" formation for the adsorption of DTAB on hydroxyapatite. They suggested that the large DTA⁺ headgroup probably prevents the chains of the adsorbed surfactants from interacting.

Figures V.11 and V.12 show a comparison of the elctrokinetic- and adsorption isotherms of DTAB-coal and HPB-coal systems respectively. It is clear from this comparison that electrokinetic isotherms cannot be used to estimate the adsorption density directly. Reasons for the remarkable constancy of the zeta potentiak even when the adsorption density continues to increase, make be caused by a displacement of the surface of shear upon further surfactant adsorption, partially cancelling the effect of added positive charge on the surface, or by an ion pair mechanism as suggested by Kosman and Rowell (105). Figure V.ll. Comparison of the adsorption and the electrokinetic isotherms for DTAB-coal system. \triangle adsorption pH 7.8 ± 0.1, \bigtriangledown zeta potential pH 8.6 ± 0.1.

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Figure V.12. Comparison of the adsorption and the electro-'kinetic isotherms" for HPB-coal system. \bigtriangledown adsorption pH 10.0 ± 0.1, \Box zeta potential pH 9.8 ± 0.1.

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V.6 Conclusion From'the discussion in the previous sections, it seems , that surfactant adsorption on /coal cannot be 'explained by a "hemi-micelle" formation mechanism as used for the case of various oxide mineral surfaces (43,46,132,135-139). The relative constancy at a given pH of the surfactant concentration at zero charge, sczc, for the C_{12} , C_{14} and C16 pyridinium surfactants leads us to believe that the surfactant alkyl chain finds enough space on the coal surface to adsorb completely. From a comparison of the electrokinetic- and adsorption isotherms, it appears as if after a certain surfactant concentration is reached either (I) the plane of shear is displaced or (2) the surfactant adsorbs as an ion pair, when the concentration of the surfactant increases beyond this "critical" concentration. Furthermore, given the relatively low value of the apparent surface as calculated from the adsorption isotherm. of phenol (Chapter V), a compound which might find relatively less abundant sites for adsorption, and the fact that surfactant adsorption density increases at pH > iep, F, it does seem that additional surface to accommodate the alkyl group is available. Thus adsorption of the cationic surfactants may indeed involve both electrostatic (headgroup) - and hydrophobic (alkyl chain) bonding to the coal surface. In addition, because charge reversal of a negatively 'charged 'coal surface occurs at a higher surfactant concentration for DTAB than DPC, it seem as if

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the arómatic ring plays at least some part in the adsorption mechanism of these surfactants, possibly through π -electrons interaction with the coal surface. This is further substantiated from adsorption data (Figure IV.27). As such, surfactant-surfactant interactions do not influence the adsorption of surfactant on -200 mesh coal as they do on mineral oxide surfaces.

Finally, Figure V.13 illustratés a possible mechanism of adsorption of a cationic surfactant on a coal surface and a typical mineral surface. If the alkyl chain of the surfactant does indeed lie flat on the coal surface, as shown in Figure V.13(a), this could imply that adsorption of these cationic surfactants on the coal surface, even at pH * iep, does not improve the hydrophobicity of the coal surface. Hence DTAB, DPC, TPB and HPB will probably be poor dewatering aids as well as poor collectors in -200 mesh coal flotation operations. On the other hand, ionic surfactant adsorption on a charged mineral surface probably occurs with the surfactant alkyl chain oriented away from the surface, towards the water phase. This is possible if • the polar sites separation is .not large enough to accommodate the tail of the surfactant (Figure V.13(b)).' In such a case, "there is an increase in the hydrophobic" mineral, and , surfactant-surfactant character of the interaction or "hemi-micelle" formation may occur. We could expect an increase in the flotation properties of the mineral (33,34,161).

Figure V.13. Adsorption of a surfactant on (a) coal surface J.

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(b) mineral surface.



CHAPTER VI

STREAMING POTENTIAL MEASUREMENTS OF COAL PARTICLES

VI.1 Introduction

, As previously mentioned, considerable attention has been devoted, in recent years, to the use of electrokinetic methods, particularly electrophoresis and streaming potential measurements, to detect modification of mineral surfacés, for example quartz, hydroxyapatite, corundum, etc. (110, 135 - 139, 150, 160).These methods are being increasingly (applied to coal surfaces as well (30,69-Because of experimental limitations, for 71,145,148,149). instance gravitational settling, microelectrophoresis is normally employed to obtain the zeta potential of small coal particles, typically in the micron range (71,145,156). Streaming potential measurements are normally performed on much larger particles, for instance +80 mesh or larger mesh size (30,110,148,149).

In Chapter V, we reported the zeta potential measurements on fine coal (-200 mesh), in aqueous solutions of various cationic surfactants and of varying pH, by means of a microelectrophoresis technique. In brief, we found, that the variation of the isoelectric point did not follow the pattern of chainlength dependence from the electrokinetic isotherms as found by Fuerstenau, Somasundaran and Healy, (137-139) for quartz- and alumina-

surfactant systems (section V.3). We suggested that, perhaps these cationic surfactants find enough space available on the surface of the -200 mesh coal and hence lie with the hydrocarbon tail along the coal surface rather than away from it.

In this chapter, we report the zeta potential measurements of coarser size coal particles (-28 + 35 mesh) by the streaming potential technique and compare the results with those obtained by microelectrophoresis (Chapter V) on a smaller size fraction (-200 mesh) of the same coal. Hence, we discuss the effect of particle size on zeta potential and the relation between electrophoreticand streaming potential methods for measuring zeta potentials of coal particles.

VI.2 Review for related studies

Sections V.3 and V.4 discuss the theory describing the influence of surfactant adsorption on the zeta potential of colloidal particles and the relevant literature. However, the comparison of zeta potentials of particles as measured by streaming potential or by microelectrophoresis has not. been examined. Irreversible thermodynamics (section IT.5) shows uneqivocally the relation between streaming potential and electroosmosis, independent of experimental variables "such as void fraction, surface conductance, etc. Overbeek (40) concluded that equation TI.18 can be applied to porous plugs provided that the surface conductance is zero. As, Hunter (46) pointed out, this also requires that the liquid

flow through the porous plug be linear and laminar and some caution is advisable since streaming potential measurements require the application of an external pressure. Although turbulence is not a problem under normal conditions, nonlinearities occur very readily in porous media. Furthermore, the treatment of electrokinetic phenomena in a porous plug presents some problems in situations where surface conductance becomes of importance, for instance.at low electrolyte concentrations. This situation is. discussed in considerable length by Dukhin and Derjaguin (47) and an excellent summary of the literature is given there. Nevertheless, we will present a brief discussion of the problems associated with the measurement of streaming potentials. There has been considerable controversy as to the agreement to be expected between the relative speeds of movement" of a solid and a liquid when such speeds are measured by the various electrokinetic methods. Similarly, there has been difficulty in assessing the effect of particle size on the electrokinetic potential.

In a review of the measurement of streaming potentials, Fuerstenau and Ball (162) discussed the problems for instance of the choice of the ratio E/P in 'equation II.18 and concluded that if these are ignored, the measurements can lead to erroneous conclusions. The proper choice of the ratio E/P in Equation II.18 is very important in determining the zeta potential. Somasundaran as well as Campbell (30,163) obtained the E/P value by dividing the

numerical value of E by the corresponding numerical value of P. It was found that the numerical E/P ratios were not constant under a given set of conditions but varied with the pressure difference, particularly at low values. It was also found that in many cases, the E/P ratios were different for the two liquid flow directions (162,163). Other authors (110,111,150,164) have chosen to use the slope, as indicated by Equation II.18, of a plot of streaming potential, E versus pressure, P. In most cases, although the plots were linear, they did not pass through the origin. Also the streaming potential observed when the liquid flowed in one direction was not the same when the flow was reversed although, in general, the slopes of the E versus P plots were usually similar. These occurrences seem to be the rule rather than the exception and have been explained in terms of an asymmetry potential between the inert electrodes used in the streaming potential measurements.

The effect of particle size on the streaming potential has also been studied in order to test the range of applicability of Smoluchowski's equation. In addition, the following important question can also be clarified: "Do the properties of the surface really remain invariable on crushing the solid, or is the "real" zeta potential a function of particle size"? A long time ago, Bull and Gortner (165) measured the streaming potential on several fractions of quartz powder at constant electrolyte

concentration. They concluded that the streaming potential increases as the particle size increases up to about 100 microns and then remains constant. Dukhin and Derjaguin (47) suggested, that the dependence of the streaming potential on particle size did not signify a violation of the principles of Smoluchowski's theory, but rather reflected the growth of the influence of surface conductance with decrease in the average pore radius. A study of the literature reveals at least four different approaches to calculate the zeta potential from streaming potential data under the influence of surface conductivity. The first attempt to tackle, this problem was made by Briggs (166) who suggested that, for the case of porous plugs, the streaming potential is proportional to the specific. conductivity, κ_n , of the liquid in the pores rather than the specific conductivity; κ , of the bulk solution. The difference between κ_{n} and κ is referred to as the surface conductance, κ_s . Hence according to Briggs*(166), the "true" zeta potential, Strue, is related to the zeta potential, CSm, calculated from equation II.18 by

 $\zeta_{\text{true}}^{\zeta} \text{Sm} = \kappa_{p}/\kappa = 1 + \kappa_{s}/\kappa$ (VI.1)

Ghosh (167,168) suggested true is related to ζ_{Sm} by

 $\zeta_{true}/\zeta_{Sm} = 1 + \alpha \kappa s/\kappa$

where α may be considered as a constant to be determined if the quantity of material and the diaphragm packing remains

(VI.2)

invariable. Roy (169) measured electroosmosis and surface conductance on four quartz powder fractions (49,56,89,124 μ m) and the sedimentation potential on two large fractions of the same powder (89 - 105 μ m, 172 - 211 μ m). He reported that the values of ζ calculated from Smoluchowki's equation and of ζ calculated from Ghosh's equation (equation VI.2) proved to be very close. In general, Pukhin and Derjaquin (47) stipulated that the calculation of ζ on the basis of electrokinetic measurements in porous diaphragms complicated by surface conductance is useful only when equations VI.1 and VI.2 have been proved valid for each concrete case.

To summarize, a study of the literature reveals at least four different approaches to calculate the zeta potential from streaming potential data under the influence of surface conductivity. Some authors (170-173) suggest that in cases involving the complicating influence of surface conductance, ζ cannot be calculated exactly by electrokinetic measurements on porous diaphragms. Others (170,174) suggest that the geometry of the pore space is also an important contributing factor in ζ -potential calculation from streaming potential data and that depending on this geometry, equation VI.1 may be either close or far from the truth. On the other hand, in determining the zeta potential of mineral- and coal surfaces, most investigators (30,111,149,150,173) have ignored the surface conductance or have mentioned that in

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these systems, the surface conductance is negligible. VI.3 Results and Discussion.

Figures VI.1 - VI.5 show the effect of flow on the potential measured between platinum electrodes separate by a packed coal plys in the presence of 10⁻⁴ m NaCl (Figures VI.1 and VI.2) and in the presence of both salt and surfactant (Figures'VI.3 - VI.5). The measurement of the streaming potential has already been described (section III.5.2). The recorder is turned on at (1) and the liquid is allowed to flow through the cell with the coal porous When the potential is stable at (2), plug (Figure III.2). the flow is stopped and the pressure is noted. The corresponding streaming potential is the difference between (2) and (3). The flow in one direction, say left to right, is resumed for several pressures and the corresponding. streaming potentials are recorded. The flow is reversed. and the process is repeated. From the results, typically shown in Figures VI.1 - VI.5, plots of streaming potentials versus pressures, as shown in Figures VI.6 - VI.10, are obtained.

Typical examples of the streaming potential versus pressure plots are shown in Figures VI.6 - VI.10. The plots are generally linear and the shopes remain the same within experimental error upon reversal of the direction of the flow of the solution (110,111,162,176). In addition, the straight lines do not extrapolate through zero potential at zero pressure. This is a common observation

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Figure VI.2. Streaming potential of coal plug in $10^{-4}m$ NaCl. pH = 10.1 ± 0.1. (a) flow right to left, R \rightarrow L, (b) flow left to right, L \rightarrow R. Negative surface of shear.



Figure VI.3. Streaming potential of coal plug in DTAB. pH = 7.9 \pm 0.1. m_{DTAB} = 3.24 x 10⁻⁵; m_{NaC1} = 10⁻⁴. (a) flow right to left, R—L, (b) flow left to right, L—R. Surface of shear negative.

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Figure VI.4. Streaming potential of coal plug in HTAB. pH = 5.4 ± 0.1. $m_{HTAB} = 2.74 \times 10^{-4}$; $m_{NaCl} = 10^{-4}$. (a) flow right to left, L \rightarrow R, (b) flow left to right, L \rightarrow R. Surface of shear positive.



Figure VI.5. Streaming potential of coal plug in HTAB. pH = 9.6 \pm 0.1. m_{HTAB} = 2.74 x 10⁻⁴; m_{NaCl} = 10⁻⁴. (a) flow right to left, R \rightarrow L, (b) flow left to right, L \rightarrow R. Surface of shear positive.

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Figure VI.6. Streaming potential of coal plug as a function of driving pressure at different pH. \bigcirc pH 5.1 ± 0.1, \bigtriangledown pH 6.3 ± 0.1, \bigcirc pH 7.7 ± 0.1, \triangle pH 10.6 ± 0.1. Open symbol: right—>left flow; closed symbol: left—>right flow. NaCl conc. 10^{-4} m.



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Figure VI.7. Streaming potential of coal plug with surfactant solution: DTAB. O pH 5.3 \pm 0.1, O pH 7.5. \pm 0.1, Δ pH 10.3 \pm 0.1. Open symbol: right—>left flow; closed symbol: left—>right flow. m_{NaCl} = 10⁻⁴, m_{DTAB} = 6.48 x 10⁻⁴.

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surfactant solution: DPC. O, pH 5.5 ± 0.1, O pH 7.0 ± 0.1, A pH 10.1 \pm 0.1. Open symbol: right —> left flow; closed symbol: left \rightarrow right flow. $m_{NaCl} = 10^{-4}$, $m_{DPC} = 3.52 \text{ x}$, 10⁻⁵.

Figure VI.8. Streaming potential of coal plug with



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Figure VI.9. Streaming potential of coal plug with surfactant solution: HTAB. O pH 5.4 \pm 0.1, \bigtriangledown pH 6.4 \pm 0.1, \bigcirc pH 7.7 \pm 0.1, \triangle pH 10.4 \pm 0.1. Open symbol: right-->left flow; closed symbol: left-->right flow. m_{NaCl} = 10⁻⁴ m_{HTAB} = 1.37 x 10⁻⁵.



Figure VI.10. Streaming potential of coal plug with surfactant solution: HPB. O pH 5.4 \pm 0.1, \bigtriangledown pH 6.7 \pm 0.1, \bigtriangleup pH 10.4 \pm 0.1. Open Symbol: right —> left flow; closed symbol: left —> right flow. m_{NaCl} = 10⁻⁴, m_{HPB} = 1.30 x 10⁻⁴.



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with this method (111,162,175) and has been attributed to the asymmetry potential of the electrodes used. In our case, this asymmetry potential was rather small, usually < 10 mV. As the recorder is turned on, a "no-flow" potential, i.e. a potential when no liquid flows through the porous plug, is observed. This potential is usually small (< 10 mV) and constant, as indicated by the fairly constant baseline in Figures VI.1 - VI.5. As the liquid flows through the coal plug, an increase in potential is observed, as described earlier. This increase in potential is taken to be the streaming potential and the so-called "no-flow" potential is neglected in the calculation of the Heta potential from streaming potential data. High driving pressures were also avoided so as to minimize turbulent flow through the porous plug. We feel that in determining the zeta potential, it is necessary to determine streaming potentials at several pressures and use the true slopes of the lines rather than the method of measuring the streaming potential at constant pressure as used by Somasundaran and Campbell (30,163).

It is also useful to discuss the errors involved in the actual determination of ζ . As indicated from equation II.18, the value of ζ depends not only on the slope of the E vs. P plot but also on the specific conductance, κ . At low pH, typically pH < 4, the observed streaming potential of the coal plug is < 0.2 mV and not stable. Thus it is difficult to measure the streaming potential of the coal

plug at pH < 4. As a result, The lowest pH ζ -potential values were obtained for the coal plug at the natural pH, i.e. pH 4.3 - 4.7. At extremely high pH (pH > 10), the conductance of the bulk solution is high, while the observed streaming potential of the coal plug is low, typically say for 6.48×10^{-4} m DTAB in 10^{-4} m NaCl, adjusted to pH = 10.3 by adding NaOH, the measured $\kappa = 1.99 \times 10^{-4}$ ohm⁻¹ cm⁻¹, while the observed conductionce streaming potentials were between -1.5 and -0.1 mV at the various driving pressures applied (Figure VI.7). The calculated g-potential at this pH is -4 mV (Figure VI.12), but because the measured streaming potential is very small, the error in the calculated g-potential is as much as ± 2 mV for this measurement at this pH. , However, between pH 4.5 and 10, the error in the calculated c-potential is small since the streaming potentials observed in this pH range were rather large, for instance for 3.24×10^{-5} m DTAB in 10^{-4} m NaCl, $\kappa = 3.95 \times 10^{-5}$ ohm⁻¹ cm⁻¹ at pH 7.9 and the observed streaming potentials were between -22.0 and -39.0 mV (Figure VI.3). The calculated g-potential is about -13 mV and the error in this particular measurement is about ± 0.5 mV. As a result, we feel that the conductance increase caused by pH adjustment limits the accuracy of the z-potential at low pH (pH < 4) and at high pH (pH > 10) for the coal porous plug. Campbell's work, which represents perhaps one of the few thorough investigations of the streaming potentials of Pittsburg

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bituminous coals (30), does not discuss the error in the calculated ζ -potential although at the limits of the pH range covered, this author used observed values of 0.1 mV for observed streaming potentials of coal in calculating the ζ -potential. In spite of this, we found the measurement to work reasonably well between the natural pH of the coal surfactant suspension and pH 10 and indeed because of associated corrosion problems, we feel that, at present, the ζ -potential of the coal particles at extremely low and high pH may not be important in terms of coal beneficiation.

Figure VI.11 shows a comparison of the zeta potentials as determined by microelectrophoresis on the coal fines ground to -200 mesh size, and the zeta potential of -28 + 35 mesh coal fraction as determined by streaming potential both in 10^{-4} m NaCl, as a function of pH. The isoelectric points, pH 5.3, as determined by both methods coincide. Independent of model considerations the two methods would be expected to yield the same isoelectric points for particles of the same coal differing only in particle size. As with the finer -200 mesh coal, the larger -28 + 35 mesh coal is positively charged in conductivity water at its natural pH of 4.3 - 4.7 and H^+ and OH^- ions are again potential determining ions (30,145). However, the zeta potential of the larger particles, as calculated from equation II.18, appears to level off at a value of about \div 18 mV for pH > 7, while the zeta potential of the small

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Figure VI.11. Comparison of the zeta potentials determined by different electrokinetic techniques on the same coal. Δ -200 mesh, microelectrophoresis; O -28+35 mesh, 'streaming potential. m_{NaCl} = 10⁻⁴.

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particles as determined by microelectrophoresis continues to decrease to a value of about -67 mV at pH 12. The large difference in the magnitude of the ζ-potential can be explained in terms of either a surface conductance effect or a "real" particle size effect, if we assume that both methods measure the same potential at the same surface of . shear. If we simply ignore the effect of surface conductance as done by several researchers (30,111,149,150, 173), as previously discussed, then the difference in the zeta potential would indicate a difference in surface properties and surface functional groups for the external surface of the larger and smaller particles. From Figure $\zeta_{\rm EP}/$ $\zeta_{\rm SP}$ at say pH 9 is about 3.2. On the other VI.11, hand, if we assume that this difference is caused by a surface conductance effect, as proposed by Briggs and others (166-168,172,177), then from equation VI.1, at pH 9, the ratio of $\kappa_{\rm S}/\kappa$ needed to explain this difference would have to be about 2.2. Such large ratios for κ_s / κ have been reported for quartz particles by Ghosh (167,168) and for thorium oxide by Holmes (177). If this is indeed the case, then the large deviation in ζ_{EP} and ζ_{SP} may be explained in terms of a surface conductance effect.. It should also be noted that the surface conductance effect is slight around the iep (Figure VI.1) but it becomes important at pH > iep. Even if the magnitude of the streaming potential of the larger coal particle would be controlled by surface conductance of the particle, the iep

and the pzr (in the case of surfactant adsorption) should not be affected. In other words, if the mechanism of surfactant adsorption on the large and small coal particles are similar, then the pzr as determined by either electrophoresis or streaming potential should be the same, again assuming that both techniques measure the same potential at the same surface of shear. In the following figures we will give ζ -potentials on coal-surfactant systems as calculated from streaming potential data using the simple equation II.18, i.e. not taking into account surface conductance as discussed above.

Figures VI.12 and VI.13 show the effect of adsorption of DTAB and DPC on the electrokinetic potential of the larger coal particles (-28 + 35 mesh) while the effect of HTAB and HPB adsorption is shown in Figures VI.14 and Also Figure VI.16 shows the surfactant VI.15. concentration dependence, at a pH well in excess of the iscelectric point (pH = 8), for DTAB, DPC, HTAB and HPB, again all in 10 $^{-4}$ m NaCl. As mentioned previously, the coal is negatively charged at pH = 8 (ζ = -44 mV from electrophoresis, $\zeta = -18 \text{ mV}$ from streaming potential). It is clear from these figures that hexadecyltrimethylammonium and hexadecylpyridinium adsorption leads to charge reversal at a pH well above the isoelectric point even for very low 'surfactant solution concentrations (around 10^{-5} m). In the case of dodecyltrimethylammonium and dodecylpyridinium adsorption at pH 8 or above, charge reversal takes place





Figure VI.13. Zeta potentials of coal in the presence of DPC from streaming potential data. O = 0; $\Box 3.52 \times 10^{-5}$ m; $\triangle 3.52 \times 10^{-4}$ m; $\Diamond 3.52 \times 10^{-3}$ m. m_{NaCl} = 10^{-4} .





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Figure VI.14. Zeta potentials of coal in the presence of HTAB from streaming potential data.O- 0; $\triangle 1.37 \times 10^{-5}$ m; 1.37 x 10⁻⁴ m; $\triangle 2.74 \times 10^{-4}$ m. m_{NaCl} = 10⁻⁴.

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Figure VI.15. Zeta potentials of coal in the presence of HPB from streaming potential data. $\bigcirc -0$; $\checkmark 2.60 \times 10^{-6}$ m; $\blacktriangle 1.30 \times 10^{-5}$ m; $\blacksquare 1.30 \times 10^{-4}$ m; $\bigtriangleup 2.60 \times 10^{-4}$ m. m NaCl = 10^{-4} .



Figure VI.15: Variation of zeta potential of coal with , concentration of alkylpyridinium surfactants at constant pH. \bigcirc DTAB, \square DPC, \bigtriangledown HTAB, △ HPB. pH = 8.0. m_{NaCl} = 10⁻⁴. Arrow: zeta potential in absence of surfactant.



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only at much higher surfactant solution concentrations, typically 10^{-3} m. This observation, therefore, again invites a comparison to the results of Fuerstenau, Somasundaran and Healy and others (137,138,152,159, section V.3) for the chainlength dependence of ionic surfactant adsorption on charged mineral surfaces. If we compare the surfactant concentrations at the p'zr (Figure VI.16) of this coarser coal, i.e. log c = -5.2 for HPB and HTAB, and about -3.2 for DPC and DTAB, this leads, following equation V.3, to a free energy of surfactant-surfactant interaction of .1.1 kT per CH₂ group added to the chain. Furthermore, it seems as if the headgroup of these cationic surfactants, has little or no effect on the surfactant adsorption on the larger coal particles (Figures VI.12 - VI.15). In contrast, we found a minor but definite cationic surfactant headgroup influence on its adsorption on the finer -200 mesh coal particles and explained this in terms of an interaction between the pyridine ring and the coal surface (section V.5.2.2). If we assume that both streaming potential and microelectrophoresis measure the same potential at the same surface of shear, there is perhaps a particle size effect which must be taken into consideration when studying the role of surfactant adsorption on coarse coal particles.

We should therefore be cautious about the application of the Fuerstenau, Healy and Somasundaran model (section V.3) to the present case of surfactant adsorption on coal.

It is our opinion that whether or not the chainlength dependence of surfactant adsorption should be attributed to a hydrophobic interaction between the chains rather than to a hydrophobic interaction with the solid surface will depend on local surface conditions. For instance, in the case of surfactant binding by polyelectrolytes, where the binding sites are very close, it seems reasonable to attribute the 1.1 kT factor observed to the hydrophobic interaction between neighbouring chains, similar to the case of micelle formation (96,178). In the case of coal, it is possible that the surfactant molecules adsorb on the surface of very fine coal particles (-200 mesh) with the tail lying flat on the surface while in the case of the surface exposed by larger coal particles (-28 + 35 mesh) the surfactant adsorbs with the tail away from the surface and thus the l.l kT factor is indeed the surfactantsurfactant hydrophobic interaction. On the other hand, it is possible that the surfactant molecules do adsorb with the tail lying on the coal surface and the l.l kT factor obtained from the streaming potential data is simply a result of Traube's rule. In either case such an interpretation of the streaming potential and electrophoresis data would indicate a definite difference between the properties of the exposed surface of large coal particles and very fine particles ground from the same coal, leading to different electrokinetic and surfactant adsorption behavior.

In order to improve our understanding of the coalsurfactant system, considerable experimental work, based on different experimental techniques on the same coal to provide accurate data, is needed. From our study, it seems that, if we neglect surface conductance effects as usually done in coal-electrokinetic studies (30,111,149,150,173), electrophoresis and streaming potential measurements do not yield similar absolute *z*-potential values for the same coal of different particle size. This problem can only be clarified if the complicated issue of surface conductance, especially of coal systems, is studied more thoroughly. Nevertheless, irrespective of the absolute value of ζ being similar from both electrokinetic technique, with or without a surface conductance effect, the pzr, in the presence of surface active agents, of coal should be the same as measured by electrophoretic- or streaming potential methods. Thus when we notice remarkable differences in the pzr in various surfactant systems for the -200 and the -28+ 35 mesh fractions, we conclude that our study shows that the adsorption mechanism as determined from the electrokinetic behavior of coal-surfactant systems might depend on particle size. As such, perhaps the essential criterion in understanding coal-surfactant interactions might be the change in *z*-potential and not the absolute value of the zeta potential and hence surface conductance effects might after all not be important.

CHAPTER VII

SUMMARY AND CONCLUSION

The work described in this thesis represents an experimental investigation of the surface properties of fine coal in aqueous surfastant solutions. . Because of increasing energy demands and escalating prices for oil and gas, coal has become an increasingly attractive fuel to meet the energy needs of the present and future society. Yet increased coal utilization is progressing only slowly, in large part because of the stringent environmental constraints. At present, SO2 emissions are high and must be reduced if coal is to be an environmentally acceptable Recent studies indicate that to liberate 50 percent fuel. ash in coal, the material must be ground finer than 60 µm. In addition, improved technology in coal mining has led to more coal-fines and ultra-fines being in the product As a result, fine coal cleaning will be an stream. important aspect of coal preparation in the future use of coal as a fuel. This means that more research needs to be 'done on processes which can beneficiate fine coal particles and coal containing a high percentage of sulfur. Fine coal beneficiation can perhaps best be achieved by the utilization of methods which exploit the differences in the surface chemistry of the coal and associated mineral matter. These surface dependent processes include froth

flotation, agglomeration and selective flocculation.

It is primarily because of this that coal-surfactant systems are of interest to the colloid chemist especially from an experimental point of view. Of course, the study of the modification of the coal surface by adsorption of surface active agents falls within the realm of colloid chemistry even though the coal particle size may, in most cases, be greater than colloidal dimensions. This dissertation therefore attempts a systematic investigation of the surface properties of fine coal using the principles of colloid chemistry.

A general introduction to coal chemistry and mineralogy is given in the first chapter. This chapter" also looks at the problems associated with coal combustion. The important conclusion drawn from this chapter is that, in spite of its impending importance, little work has been done on the study of the surface properties of the coalwater interface with the long term goal of improving coal beneficiation processes.

Chapter II presents a review of some of the relevant basic equations of colloid chemistry to be used in this research. These include the theory of adsorption from solution on a solid, the theory of the double layer, and the determination of zeta potential (double layer electric potential at the surface of shear) from electrophoresis and streaming potential measurements. The application of these equations, generally used in other areas of colloid

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science, to the coal-solution interface is discussed in the later chapters. Chapter III describes the experimental part of this investigation. It includes the methods of analyses of the coal used, free surfactant concentration determinations, which includes a description of a novel surfactant ion selective membrane electrode used to measure free cationic surfactant concentrations and electrokinetic methods of methods of methods.

Adsorption of the various surface active agents on a finer -200 mesh coal fraction is described in Chapter IV. The results indicate that the adsorption of cationic surfactants not only increases as the pH of the coal suspension increases, i.e. as the surface of the coal becomes more negatively charged, but also as the hydrophobic chain of these surfactants also increases. From, this we conclude that cationic surfactant adsorption involves both an electrostatic- (surface charge) as well as a hydrophobic interaction between the surfactant and the coal surface. Surface areas and free energies of adsorption based on phenol adsorption are also presented in this chapter. Because of the porous nature of coal, it is difficult to have a real standard for surface area. determinations. Researchers in coal chemistry have often used adsorption of either CO₂ or N₂ for surface area determinations of coal. As shown in most cases, the mechanism of gas adsorption on coal is not the same as

adsorption from solution, since in solution the water molecules will also compete for the active sites on the coal surface. Although equilibrium conditions are not met, we have used adsorption of phenol from water as the standard in surface area determination of the coal used in this study. Phenol is a simple molecule whose mechanism of adsorption has been long studied on carbon, and recently on coal by some resarch groups. Finally, this chapter describes a novel technique of free cationic surfactant concentration determination. Although limited by the pH of the suspension, the surfactant ion selective membrane electrode is useful in that it can measure free surfactant Removal. concentration in the presence of the coal fines. of the coal fines is not necessary prior to concentration determination as with other methods presently used. Hence, this electrode can be useful in say flotation cells to monitor free surfactant concentration during various flotation stages. We have used surfactants of an extremely high purity in this study but we feel that the membrane electrode may work in the presence of a mixture of surfactants. We have also found that the response of the electrode is not affected by excess salt and so its use can be further extended in coal suspensions normally associated with excess salt.

Chapter V discusses the effect of surfactant adsorption on the zeta potential, as determined by microelectrophoresis, of -200 mesh coal. The results of this

investigation are compared to a generally accepted model of ionic surfactant adsorption on mineral surfaces. From this study, we concluded that the mechanism jof surfactant adsorption on fine coal is not the same as on other mineral surfaces, for instance quartz and alumina. We found that although cationic surfactant adsorption causes a charge reversal of the coal surface at pH > iep at extremely low surfactant concentrations, there is essentially no difference in the surfactant concentration at zero charge for a C_{12} surfactant compared with a C_{16} surfactant. On the basis of zeta potential and adsorption measurements, we proposed that at pH > iep, the cationic surfactant is adsorbed at low concentrations by an electrostatic mechanism but with its hydrophobic tail along the surface of the coal, instead of away from the coal surface into the aqueous phase as suggested in the case of other minerals. As a result, the coal may still not be quite hydrophobic as in the case of other minerals. If this is indeed the case then use of these surfactants in flotation circuits would probably not improve the flotation of this coal even at pH > iep. Preliminary microflotation experiments not described in this thesis show that use of these surfactants as collectors does not improve the flotation of a poorly floated -200 mesh coal. However, systematic flotation studies must be carried out using these surfactants as collectors before a definite answer can be given as to the usefulness of these particular surfactants as collectors.

It must also be remembered that because of the ionic charge of these surfactants, they will also have an affinity for the gangue usually associated with the coal. By effectively studying the surface properties of the coal and the gangue, it will be possible in the future to make the coal surface and the gangue oppositely charged by varying the pH of the suspension.

Finally Chapter VI examines the effect of cationic surfactant adsorption on the zeta potential, as measured by a streaming potential technique, of the same coal but of a larger particle size. Since fines circuit stream will inevitably contain coal fines of different particle sizes, we feel that it is equally important to investigate the effect of particle size on the mechanism of surfactant adsorption. From suggested model calculations for ionic surfactant adsorption on minerals, for example quartz, it appears as if surfactant adsorption on coal of -28 + 35 mesh size occurs with its hydrophobic tail oriented towards the aqueous phase. At high surfactant concentration, it seems as if any hydrophobic interaction may be due mainly, to the adsorbed adjacent tail rather than the surfactant tail and the coal surface as is suggested for the finer - 200 mesh coal. However, we suggest some degree of caution in believing that this is the only possible explanation since the 1.1 kT factor might simply be a result of Traube's rule. Nevertheless, our study indicates that streaming potential and electrophoresis data suggest

that there is a definite difference between the surface properties of fine and large coal particles. If the surfactant cation does indeed adsorb on the larger coal particles with its tail oriented towards the water phase, then, according to an earlier argument, these surfactants may be good collectors in the flotation of large coal particles. No such investigations have been carried out as yet but in the flotation of larger coal particles, particle size will become a limiting factor also.

The effect of surface conductance on ζ -potential calculations has also been discussed in Chapter VI. Although we have not directly measured the surface conductance, we have discussed its effect on the magnitude of the *z*-potential. If we assume that both microelectrophoresis and streaming potential measure the potential at the same surface of thear, then our results indicate that if surface conductance is neglected, as is generally done in rg-potential calculations from streaming potential data, then particle size influences the absolute value of the ζ -potential. Irreversible thermodynamics offers a means of comparing data from various electrokinetic methods. If for instance we could study the zeta potential of coal surfaces by both streaming potential and electrophoresis then we should be able to determine the role of surface conductance in these measurements. 'Hence we feel that the effect of surface conductance on the streaming potential of coal systems should be thoroughly

studied as it may not be possible to neglect this effect in zeta potential calculations as is normally done. However, our results show that, if both microelectrophoresis and streaming potential measure the same potential at the same surface of shear, surface conductance affects only the absolute value of the g-potential but not the iep nor, in the case of surfactant adsorption, the pzr. Earlier, we mentioned that improvement in fine coal beneficiation by processes such as flotation depends on the surface properties of the coal-water interface. In the absence of complete flotation results, it is perhaps difficult to conclude as to whether the magnitude of or just the change in ζ-potential is important in the beneficiation of fine coal. To further supplement the conclusions of this work, flotation and dewatering studies on this coal-surfactant system should be carried out.

In conclusion, this investigation has offerred a further insight into the the interfacial properties of the coal-water interface. At present, it might be feasible to make broad generalizations regarding fine coal cleaning by a particular method. Eventually we hope that coal cleaning technology will reach a point where, given a certain minimum amount of information regarding a coal's surface properties, a coal's performance in a particular process can be accurately predicted. This neccesitates that more studies be done on the surface properties of the coal-water interface so that a suitable data base can be established.

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