A Reduced Adsorption Isotherm for Surfactant Mixtures

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ABSTRACT

The adsorption of surfactants of similar structure on mineral oxide surfaces can be described by a single adsorption isotherm when plotted against reduced concentration. The total adsorption of mixtures of these surfactants and the adsorption of each individual surfactant in the mixture can be estimated from this reduced adsorption isotherm. No mixture data are required for this calculation. The method of calculating the reduced concentration for pure surfactants and surfactant mixtures is discussed. Adsorption data of three isomerically pure alkylbenzene sulfonates and binary mixtures of these surfactants on alumina and kaolinite is used to illustrate this correlation.

INTRODUCTION

Surfactant adsorption on minerals is of current interest because of its importance in those processes which use micellar solutions for the enhanced recovery of oil. While the total amount of surfactant adsorbed on the reservoir matrix is of prime importance, the preferential adsorption of some surfactant species is also of concern. This selective adsorption can result in the chromatographic separation of the different surfactant types which have been blended to yield an effective oil recovery agent and, thereby, greatly reduce the efficiency of the process.

Isotherms representative of surfactant adsorption from aqueous solutions on mineral oxide surfaces can be characterized by four distinct regions. For very dilute solutions and sparse surface coverages, Henry's law is obeyed. At a critical solution concentration, the isotherm deviates markedly from linear behavior, signaling the transition from the first to the second region, with adsorption increasing rapidly as the solution concentration is increased. In the third region, adsorption increases less rapidly with increasing concentration. In the fourth region, a plateau is reached and adsorption is independent of the surfactant concentration. This plateau is generally reached at the surfactant critical micelle concentration (CMC), although it is possible to saturate the surface at concentrations less than the CMC.

A number of attempts to model surfactant adsorption have been reported. The finite layer BET model (1), the Langmuir adsorption isotherm (2-7), and the Tempkin adsorption model (2,3) have all been used to describe ionic surfactant adsorption, but none of these accurately represents the characteristic isotherm shapes. Scamehorn et al. (8) and Cases et al. (9) have developed theoretically based models which do represent real isotherm shapes. Their development assumes that hemimicelles, which are surface aggregates of surfactant molecules, form by a phase transition mechanism promoted by the lateral attraction between the surfactant's hydrocarbon tails. Scamehorn et al. (8) concluded that the surface aggregates tend to be bilayered structures and that adsorption saturation occurs prior to reaching the CMC only when bilayer coverage is complete.

The striking feature of this physical model of surfactant adsorption is the dominant role accorded lateral interactions between the surfactants' hydrocarbon tails. These are the same interactions (the hydrophobic effect (10)) responsible for the aggregation of surfactants into micelles. For these systems, almost all adsorbed surfactant is present in the form of hemimicelles (8). The change in free energy per methyl group found for micelle formation is comparable to that for hemimicelles (8,11-13). It is this similarity which is responsible for the success which reduced adsorption isotherms have enjoyed (1,9,14,15). A reduced isotherm is one in which the adsorption is shown as a function of reduced surfactant concentration, where the reduced concentration is the concentration divided by a "critical concentration"– usually the surfactant CMC. The value of a reduced isotherm lies in its generality. All surfactants of a given homologous series would yield the same reduced isotherm.

This paper develops reduced adsorption isotherms, which describe the total adsorption of a surfactant mixture. This novel application of the reduced adsorption isotherm concept requires no mixture data and only meager single surfactant system data to predict adsorption of all surfactant components in a mixture. The restriction on this model is that it is only applicable below the CMC and to surfactants belonging to a homologous series.

EXPERIMENTAL PROCEDURES

The surfactants used were: sodium 4-([3′]nonyl) benzene sulfonate (3-ϕ-C_9ABS), sodium 4-([3′]decyl) benzene sulfonate (3-ϕ-C_{10}ABS), and sodium 4-([4′]dodecyl) benzene sulfonate (4-ϕ-C_{12}ABS). These compounds, the other materials used, and the procedures employed are discussed in detail elsewhere (8).

RESULTS AND DISCUSSION

Pure Component Systems

Adsorption is plotted against reduced concentration for ABS isomers on alumina and kaolinite in Figures 1 and 2, respectively. The critical concentrations used to calculate the reduced concentrations were selected so that the adsorption data intersected the plateau adsorption value, which is observed at high surfactant concentrations, at a reduced concentration near unity, and so the data for the different isomers coincides closely on each substrate. However, since the plateau adsorption is a function of alkyl chain length (8), the reduced isotherm concept cannot be expected to apply precisely in the high concentration region.

At low concentrations, Henry's law is obeyed (8). However, this region is experimentally inaccessible for most of the surfactants in Figures 1 and 2 under the conditions used. Therefore, to test the validity of the single component reduced isotherm in the Henry's law region, adsorption data were obtained at a low solution/solid ratio (and therefore slightly different pH) as shown for

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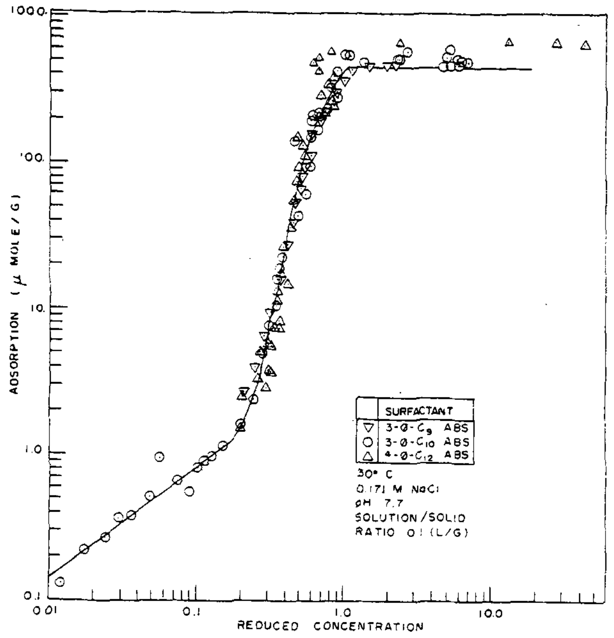

FIG. 1. Adsorption of single surfactants on alumina.

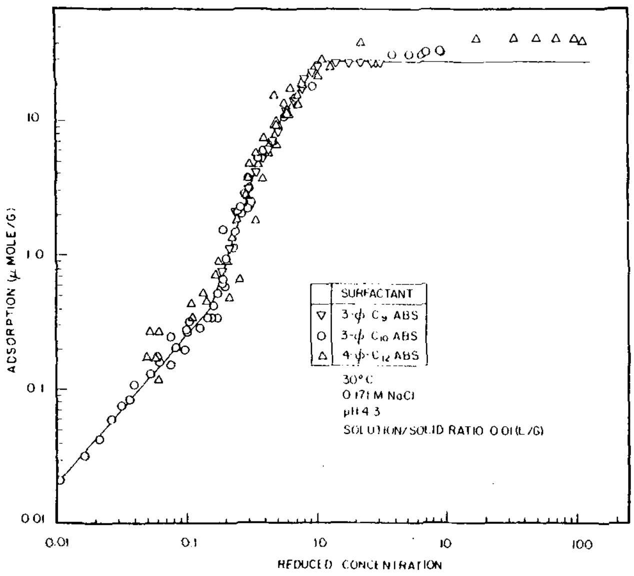

FIG. 2. Adsorption of single surfactants on kaolinite.

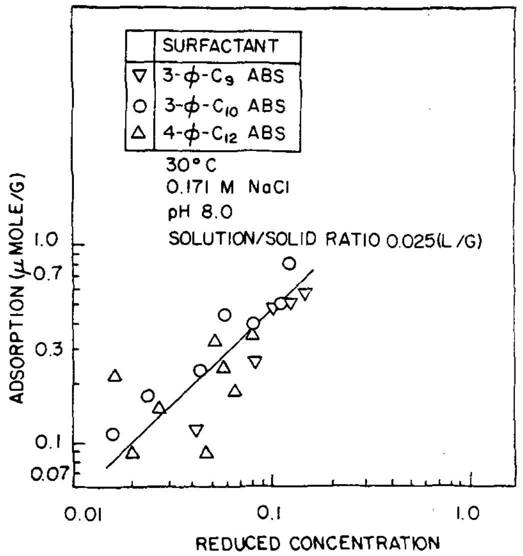

FIG. 3. Adsorption of single surfactants on alumina in the Henry's law region.

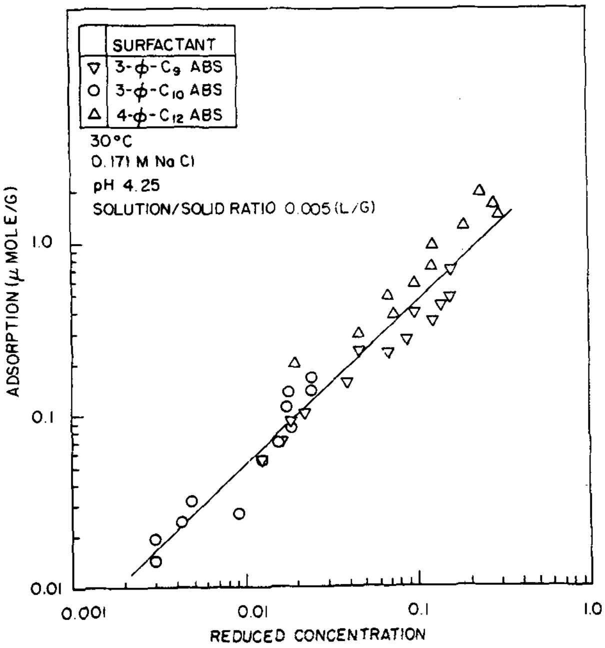

FIG. 4. Adsorption of single surfactants on kaolinite in the Henry's law region.

the two substrates in Figures 3 and 4. Since the CMC is nearly independent of pH for these compounds (8), the critical concentration is assumed to be also, and the same critical concentration is used to calculate reduced concentration in Figures 3 and 4 as was obtained from the data in Figures 1 and 2. The lines drawn in Figures 3 and 4 correspond to Henry's law (a slope of one on log-log paper) and can be seen to fit the data over a wide concentration range. Since pH affects adsorption, adsorption densities are not the same in Figures 1 and 3 and in Figures 2 and 4; but at a given pH, the reduced adsorption isotherm has been shown to describe all three surfactants used, with the critical concentration being independent of pH.

A single reduced adsorption isotherm has been shown to apply for the homologous series of surfactants being used. Reduced adsorption isotherms have been reported by other investigators (1,9,14,15). The CMC was used as the critical concentration in those studies. The critical concentrations used here represent the "best fit" (by visually adjusting the curves), and these are compared to the CMC in Table I. There is a deviation between those quantities for 3-ϕ-C_9ABS and 4-ϕ-C_{12}ABS isomers; however, the agreement between reduced isotherms found using the CMC as the critical concentration is only slightly poorer. Thus, when there is a need to minimize the number of experiments, the CMC represents an adequate choice for the critical concentration.

Surfactant Mixture Adsorption

The total adsorption of surfactant from an aqueous solution containing a mixture of surfactants is hypothesized to correspond to the same reduced isotherm as that of

TABLE I

Comparison of CMC and Critical Concentration

(μmol/L)	3-ϕ-C_9ABS	3-ϕ-C_{10}ABS	4-ϕ-C_{12}ABS
CMC	1694	727	90.4
Critical concentration (alumina)	2302	727	72.7
Critical concentration (kaolinite)	2276	727	51.8

the pure components comprising the mixture. By total adsorption is meant the sum of the adsorptions of the individual surfactants. The validity of this hypothesis depends, as will be seen, on making an appropriate choice of critical concentration and on each of the surfactants having the same reduced isotherm. This latter condition usually, but not necessarily, requires that surfactants having the same hydrophilic moiety be considered.

To define a critical mixture concentration, the similarity between micelle and hemimicelle formation is again emphasized. In the presence of a large amount of added electrolyte, the monomer-micelle equilibrium in a mixture of ionic surfactants can be represented by treating the system as a mixture of nonionic surfactants, since the electrolyte contributed from the dissociation of the surfactant is small compared to the total present; this condition was satisfied for all experiments reported here. An equation has been presented (16-18), which yields the CMC of such a surfactant mixture, assuming the micellar phase to be ideal. This same equation will be used to calculate a mixture critical concentration except that the critical concentrations of each of the pure components rather than their CMC will be used when these are different. Thus, for a n component surfactant mixture:

$$CCP_M = \frac{\prod_{i=1}^{n} CCP_i}{\sum_{i=1}^{n} x_i \prod_{\substack{j=1 \\ j \neq i}}^{n} CCP_j} \qquad [1]$$

where x_i is the mole fraction of surfactant i in the solution, CCP_i is the critical concentration for pure i, and CCP_M is the mixture critical concentration.

In this work, the term mole fraction refers to the molar fraction of the total surfactant in the phase of interest (monomer solution, adsorbed phase, or feed solution) and is not the mole fraction relative to the total number of moles of all components present. Thus, $x_1 = 0.5$ implies that half of the total number of surfactant molecules present in solution are of type 1.

The application of Equation 1 to binary mixtures of 3-ϕ-C_{10}ABS and 4-ϕ-C_{12}ABS is shown in Figures 5 and 6 on alumina and kaolinite, respectively. The data cover two different feed (solution prior to adsorption) mole fractions. It is important to note that the x_i appearing in Equation 1 refers to the final solution composition. These will generally differ from the initial composition since the adsorption of each component will generally differ.

It is seen that the agreement between experiment and theory is reasonable. Thus, the total surfactant adsorption is quite well represented by the reduced adsorption isotherm. One difficulty, which may not be immediately clear, is that to calculate the final solution concentration and mole fraction of surfactant, one requires a knowledge of the adsorption of the individual surfactants, not simply the total adsorption. Figures 5 and 6 have been constructed based on measured values of the final solution mole fractions. These can, of course, be calculated by material balances given the solution to solid ratio and a method of calculating the individual adsorptions. To obtain the fraction of each surfactant comprising the adsorbate, again we use the similarity between hemimicelles and micelles and propose that ideal mixed hemimicelles form on the surface. Thus,

$$\frac{z_i}{x_i} = \frac{CCP_M}{CCP_i} \qquad i = 1, \ldots n \qquad [2]$$

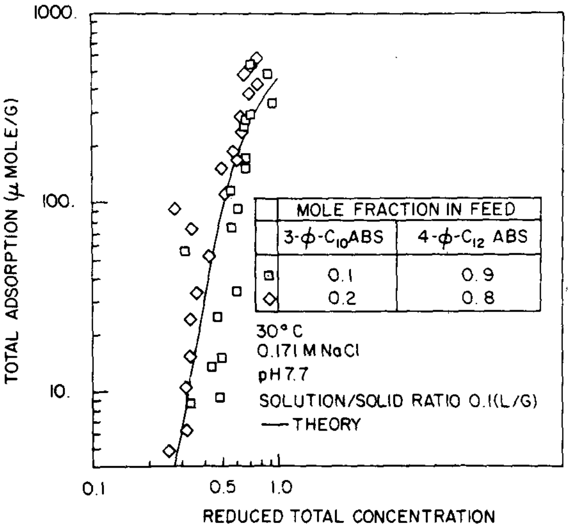

FIG. 5. Total adsorption of a 3-ϕ-C_{10}ABS and 4-ϕ-C_{12}ABS mixture on alumina.

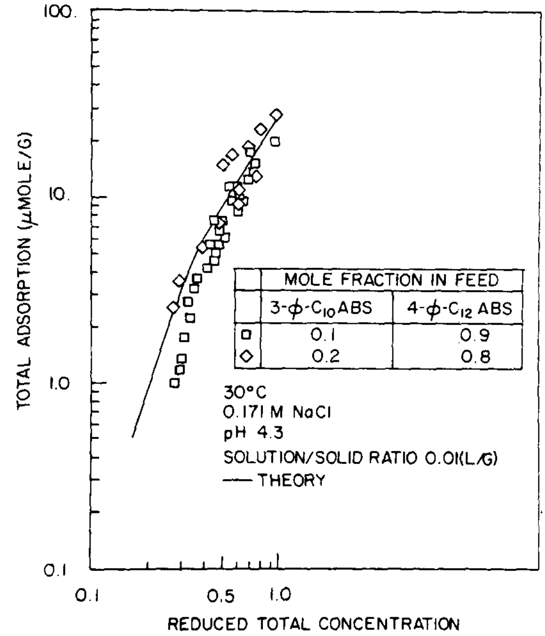

FIG. 6. Total adsorption of a 3-ϕ-C_{10}ABS and 4-ϕ-C_{12}ABS mixture on kaolinite.

where z_i is the mole fraction of surfactant i in the adsorbed phase (hemimicelles). The predicted mole fractions calculated using this equation agree satisfactorily with the observed mole fractions as shown in Figures 7 and 8. Since Equation 2 is analogous to the equation used by Mysels and Otter (19) to describe the equilibrium between surfactant monomer and micelles, the agreement is considered to be a further substantiation of the profound similarity between micelles and hemimicelles and provides further evidence for the existence of mixed hemimicelles first proposed by Scamehorn et al. (20).

It is important to note that Equations 1 and 2 allow calculation of surfactant mixture adsorption and the composition of the adsorbed phase, based solely on single component isotherms. If even less accuracy is necessary, the adsorption isotherm of one component and the CMC of each component present allow calculation of these same quantities (by assuming that the pure component critical concentration is equal to the CMC).

There are at least two constraints limiting the validity of reduced isotherms for predicting the adsorption of surfactant mixtures. The calculations as presented here apply only if the surfactant solution concentration is less than the mixture CMC. If this is the case, all of the surfactant is present as monomer. Above the mixture CMC, the mole fractions of each surfactant in the monomer are different from those in the total solution. Since adsorption then depends on the monomer concentration rather than the solution concentration (8), it would be necessary to consider monomer-micellar equilibrium and to incorporate material balances into the calculations. Trogus et al. (21) have discussed these difficulties in some detail and Scamehorn et al. (20) have demonstrated the validity of their approach. It is believed that, using this approach, the adsorption could then be calculated from the relationships given here. It is crucial to understand that the x_i are monomer mole fractions, not the solution mole fractions, for concentrations greater than the mixture CMC.

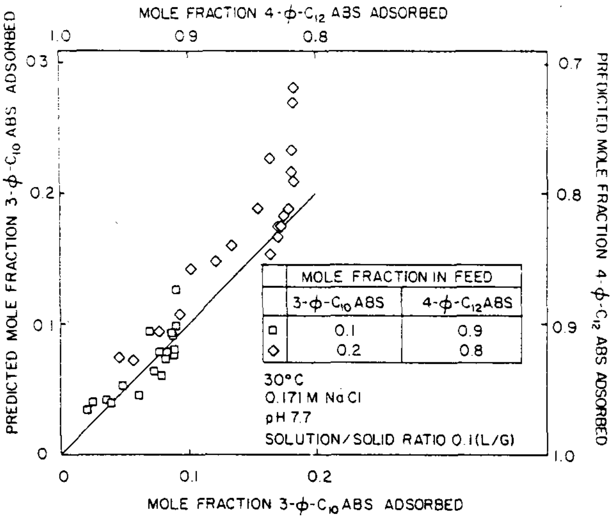

FIG. 7. Composition of adsorbed phase for adsorption of 3-ϕ-C_{10}ABS and 4-ϕ-C_{12}ABS mixtures on alumina.

A second restriction to be stressed is that although this correlation should be reasonably good for surfactants having the same hydrophilic moiety, it is uncertain how widely it may be applied. It would not, for example, apply to mixtures exhibiting strong synergistic interactions between unlike components, as for example, a mixture of anionic and nonionic surfactants (22).

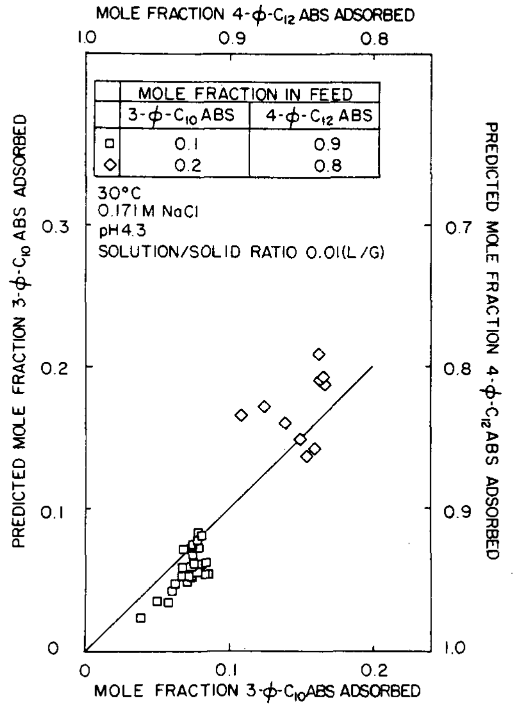

FIG. 8. Composition of adsorbed phase for adsorption of 3-ϕ-C_{10}ABS and 4-ϕ-C_{12}ABS mixtures on kaolinite.

ACKNOWLEDGMENTS

This research has received financial support from the following organizations: Amoco Production Co., Ashland Chemical Co., Atlantic Richfield, British Petroleum Co. Ltd., Chevron Oil Field Research, Conoco Inc., Department of Energy, Elf-Petroleum Corp., Exxon Production Research Co., Gulf Research and Development Co., Marathon Oil Co., Mobil Research and Development Corp., Shell Development Co., Stepan Chemcial Co., Suntech Inc., Texaco Inc., Union Oil Co. of California, The University of Texas Engineering Foundation, and Witco Chemical Corp.

Professor Schechter holds the Dula and Ernest Cockrell, Sr., Chair in Engineering

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[Received November 9, 1981]

Surfactants in Coal Technology[1]

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ABSTRACT

The principal uses of surfactants and related compounds in coal technology are the control of coal dust, the purification of coal from admixtures by flotation, the dispersion of coal in water for transportation through pipelines and as a fuel system, the dispersion of coal in fuel with subsequent burning of the coal/oil mixture, demineralization of coal, freeze-conditioning agents and side-car release agents for railroad transport of coal. These applications have been reviewed in this order. This overview demonstrates that the use of surfactants in coal technology is rapidly growing with the increasing interest in utilizing coal as a source of energy and that basic studies are in progress to explain the underlying surface chemical phenomenon.

INTRODUCTION

With the growing interest in utilizing coal as a source of energy, it seems appropriate to present an overview of the role surfactants play in coal technology. Surfactants have been used in coal technology for a considerable length of time. However, basic studies of the underlying phenomena are quite recent. With the current increasing interest in energy problems, an intensive research program on the utilization of surfactants in coal technology is in progress in many laboratories and numerous products have been developed. A classification of coals by rank is presented in Table I in decreasing order of carbon content. The principal uses of surfactants and related compounds are listed in Table II and will be discussed in this order.

Wetting of Coal Surfaces

Fuller et al. (2–4) have elucidated the heterogeneity of coal surfaces in this study of the structure and chemistry of coals. Fuller (2) has shown that calorimetric analysis is a valuable method for the investigation of the structure and chemistry of coals. Heats of immersion studies indicate that lower ranked coals imbibe more water onto more polar sites such as carboxyl, phenolic, etc., than higher ranked coals. Mineral matter reacts strongly with polar liquids such as water, giving rise to higher heats of immersion. Attack by alkali loosens the coal structure markedly to allow enhanced access to fluid reagents.

Heats of wetting of coal in liquids may be considered a

TABLE I

Classification of Coals by Rank (1)

Class	Group	Fixed carbon limits (%) Equal or greater than	Fixed carbon limits (%) Less than	Volatile matter limits (%) Greater than	Volatile matter limits (%) Equal or less than	Calorific value limits (BTU/lb) Equal or greater than	Calorific value limits (BTU/lb) Less than
1. Anthracite	1. Metaanthracite	98	–	–	2	–	–
	2. Anthracite	92	98	2	8	–	–
	3. Semianthracite	86	92	8	14	–	–
2. Bituminous	1. Low volatile bituminous coal	78	86	14	22	–	–
	2. Medium volatile bituminous coal	69	78	22	31	–	–
	3. High volatile A bituminous coal	–	69	31	–	14,000	–
	4. High volatile B bituminous coal	–	–	–	–	13,000	14,000
	5. High volatile C bituminous coal	–	–	–	–	11,500	13,000
						10,500	11,500
3. Subbituminous	1. Subbituminous A coal	–	–	–	–	10,500	11,500
	2. Subbituminous B coal	–	–	–	–	9,500	10,500
	3. Subbituminous C coal	–	–	–	–	8,300	9,500
4. Lignitic	1. Lignite A	–	–	–	–	6,300	8,300
	2. Lignite B	–	–	–	–	–	6,300

Reprinted from ref. 1, p. 6, courtesy of American Institute of Mining, Metallurgical and Petroleum Engineers, Inc.

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[1] Paper presented at the symposium on Recent Advances in Surfactant and Surface Chemistry, sponsored by the North Eastern Section of the AOCS in Carteret, New Jersey, November 19, 1981.

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