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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

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TABLE II

Surfactants in Coal Technology

Wetting of coal surfaces
Coal dust
Flotation
Coal/water dispersions
Coal/oil dispersions
Demineralization of coal
Freeze-conditioning agents
Side-car release agents

measure of reagent accessibility in coal conversion processes (5–7). The rate at which the steady state is established after wetting of the coal can be followed conveniently with a microcalorimeter. For example, Wightman et al. (5) have shown in a study of a homologous series of *n*-alcohols ranging from C_1 to C_{12} that the steady-state time increases with increasing alcohol chain length, suggesting limited penetration of the wetting liquid into the coal structure as the alcohol chain length increases with concomitant decreases in heat of wetting.

The determination of the interfacial tensions and contact angles of small coal particles with water for different types of coal are of interest in connection with processes such as the selective flotation of coal, or the inclusion of coal particles into oil droplets as a means of enriching fuels.

Methods for contact angle measurements on small, irregularly shaped solid particles have not been available in the past. Therefore, Neumann et al. (8–11) have developed a new technique for subbituminous coal particles. This method considers the behavior of the particles in the range of 25–300 μm at solidification fronts of certain solidifying melts or, in other words, matrix materials such as naphthalene, biphenyl, salol and *o*-phenyl phenol. This method interprets quantitatively engulfment or rejection of the coal particles by the solidification front of the solidifying matrix material.

According to Neumann et al. (8), thermodynamics predicts that a particle embedded in a solidifying melt will be pushed by a solidification front, if the change in free energy of engulfment is positive. However, as the solidification front velocity is increased, a limiting or critical velocity V_c will be reached at which viscous drag becomes greater than the thermodynamic repulsion and, consequently, engulfment will occur. It has been demonstrated that it is possible to obtain an empirical relationship between the free energy of adhesion of the particle to the solidification front ΔF^{adh}, the particle diameter l, V_c and other relevant system properties (10). A correlation between dimensional analysis and experimental data is illustrated in Table III, in which the data are in agreement (11).

Using this engulfing technique, Neumann et al. (9) have shown that the wetting properties of coal depend on its carbon content, ash content and mineral contamination. In addition, it was demonstrated that hydrophilic coal can be rendered more hydrophobic, which is a necessary requirement for the floatability of coal particles, by addition of surfactants.

Coal Dust

The use of aqueous surfactant solutions to improve wetting of coal particles has important practical consequences for mine dust control. Nonionic surfactants, sodium alkyl orthoxylene sulfonate and others are used in this application (6, 12–15). Glanville et al. (12) have shown that among other factors, the wetting rates as determined by the Walker wetting rate test of coal dust are strongly affected by the temperature, the size consist (composition) of coal dust, the concentration and molecular structure of the particular surfactant used. Wetting rates increase in roughly linear fashion in the temperature range from 10 to 40 C, and similarly in roughly linear fashion with increasing average particle diameter of the coal dust at a given temperature.

TABLE III

Critical Velocity (μm/sec)

System	D = 60 μm		D = 140 μm	
	DA	Expt	DA	Expt
Nylon-6,6/Naphthalene	28.9	30.0	15.6	17.5
PMA/Naphthalene	5.3	4.9	2.0	NA
PMA/Thymol	0.7	0.7	0.2	NA

DA: Dimensional analysis results.
Expt: Experimental results.
NA: Not available.

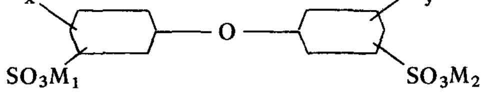
Flotation

Coal, as obtained from mining operations, is recovered in a variety of particle sizes contaminated with clay. The clay is readily washed from the surfaces of the larger coal particles, but a significant quantity of coal values of small particles is present in the coal slimes. Coal values from the clay slimes are conventionally recovered by froth flotation. This process depends largely on the difference in surface properties of the organic and inorganic components of coal (16–20).

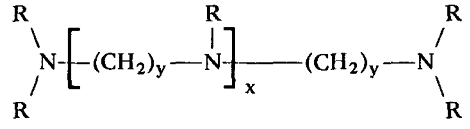
In froth flotation of coal, a froth is formed by introducing air into a slurry which contains the impure finely divided coal particles and water. The flotation separation of coal from residue or gangue depends upon the relative wettability of surfaces and the contact angle, which is the angle created by the solid/air bubble interface (16, 17).

Three general classes of reagents have been utilized in flotation processes. These are: (a) collectors or promoters, (b) modifiers, and (c) frothers. The function of collectors or promoters is to promote contact between coal particles and air bubbles by forming a thin coating over the particle to be floated, rendering the particle water-repellent. At the same time, the collector must be selective and must not coat the particles that are not to be floated. Promoters or collectors are usually kerosene and fuel oil, whereas modifiers may be pH regulators, activators, depressants, dispersants or flocculants. For example, a selective cationic polymeric flocculant is the reaction product of dimethylamine with epichlorohydrin (21).

Frothers are utilized to provide a stable flotation froth that is durable enough to facilitate the coal separation, but not so durable that it cannot be broken to allow subsequent handling. Examples of commonly used frothing agents are α-terpineol, methylisobutyl carbinol, 4-methyl-2-pentanol, 4,4-dimethyl-1-pentanol, *o*-cresol, cresylic acid, capryl alcohol and disulfonated diphenylether compounds (22, 23). The structure of the disulfonated diphenylether derivatives are given below (23):

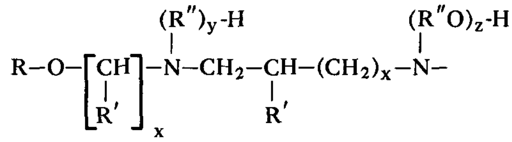


wherein R are alkyl radicals and M are alkali metals. In general, propylene tetramer is used to alkylate diphenylether, but an alkyl group in the range of C_8 to C_{20} is acceptable. Low volatile coals are easier to float than most high volatile coals. Thus. lignite is the least floatable species of coal. Cationic amine collectors are used to suppress the oxidation of coal surfaces, which changes the surface character from hydrophilic to hydrophobic. Particularly effective in enhancing the recovery of oxidized bituminous coal are condensation products of a fatty acid or fatty acid ester and a hydroxyalkylated polyalkylene-polyamine in a froth flotation process (24, 25) as shown below:



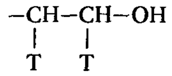
$$R_2N-\left[(CH_2)_y-N(R)\right]_x-(CH_2)_y-NR_2$$

or



$$R-O-\left[CH(R')\right]_x-N\left((R'')_y-H\right)-CH_2-CH(R')-(CH_2)_x-N\left((R''O)_z-H\right)-$$

R at each occurrence is independently hydrogen or



$$-CH(T)-CH(T)-OH$$

with the proviso that at least each T is independently hydrogen, methyl or ethyl.

In addition, oxidized coal may be concentrated by froth flotation using as a froth promoter an invertible water-in-oil emulsion of sodium polyacrylate (26, 27). The water-in-oil sodium polyacrylate emulsion inverts on usage and contact with water to an oil-in-water emulsion. An alternate method for enhancement of coal is by hydrophobic coatings formed by in situ polymerization of unsaturated monomers (28, 29).

Coal-Water Dispersions

Transport problems constitute one of the major difficulties in the use of coal. Aqueous slurries of finely ground coal containing more than ca. 55% wt solids are difficult to transport using conventional slurry pumps. As the solids level is increased above 50% wt, the water and the solids tend to separate, causing coal particles to build up in various areas throughout the pumping system. This dewatering of the slurry causes blockage and jamming of the pumping system. Moreover, it is desirable to decrease the weight percent of water in aqueous slurries, because water is a major contributor to the cost of transport and processing operation. Also, in coal gasification, a significant amount of heat is required to vaporize the water vehicle.

Let us first examine the effect of particle size on slurry stability. Funk (30) has described a coal-in-water slurry with a high coal content of 75% and a viscosity below 1000 cps, which is especially advantageous for transport by pipeline over long distances and can be burned directly without the need for dewatering at its destination. This slurry is prepared by a method wherein the particle sizes and their distribution are controlled in accordance with a particle size distribution formula which is especially beneficial for providing a novel coal compact with a minimum of void space between particles and a maximum amount of colloidal sized particles present. This compact has a particle size distribution in accordance with the Alfred formula given below:

$$\text{CPFT} = \left[\frac{D_\mu^{''} - D_s^{''}}{D_L - D_s}\right] \times 100$$

where CPFT is the cumulative weight percent, dry basis, of particles finer than particle μ of stated size, D_μ the diameter of particle μ, D_L the diameter of largest particle in compact, sieve size, or its equivalent, D_s the diameter of smallest particle in compact, SEM size or its equivalent, n the numerical exponent, with n being in the range of 0.2–1.0, and with all diameters sized in μm. This method will be more fully understood by examination of Figure 1 which is a chart showing correlations between wt % and particle size in microns of coal compacts made according to the Alfred consist (composition) formula from blends of coarse and fine fractions of Black Mesa coal and of West Virginia coal, respectively, with D_L of 70,300 and 425 μm and with $D_s < 3$ μm.

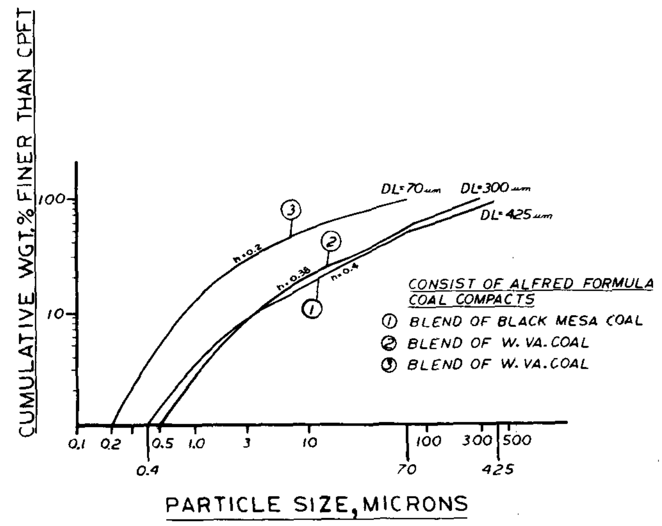


FIG. 1. Correlations between consists by wt % and particle sizes in microns of ranges of coal compacts (30).

Once the particle size distribution has been chosen for maximum solids loading, a dispersant has to be selected for minimum viscosity to reduce the interparticle network structure. Funk (30), Scheffee et al. (31), Yamamura et al. (32, 33) and Wiese et al. (34) have found that anionic surfactants are best suited for use in coal/water slurries. Scheffee et al. (31) have demonstrated in their studies that lignosulfonates are effective. Whereas sodium lignosulfonates rendered optimum dispersibility, calcium lignosulfonates rendered more stable dispersions. Funk (30) has shown that 2-ethylhexyl polyphosphoric ester acid anhydride and its potassium salt, complex organic polyphosphoric ester acid anhydride and its potassium salt, alkyl monoaphthalene sulfonic acid and its sodium and ammonium salts and mixtures thereof, particularly in combination with inorganic electrolytes such as NaOH, K_2CO_3 and $Na_2SiO_3 \cdot 9H_2O$, are effective dispersants. Proper selection of particle size distribution, dispersant and/or electrolyte render a pseudoplastic slurry of low viscosity near maximum zeta potential as shown in Figures 2 and 3. Figure 2 is a chart showing correlations between Brookfield viscosities in cps at 60 rpm and wt % coal of several Alfred formula consist of coal/water slurries identified by letters A, B, C, corresponding to those shown in Figure 1. Figure 3 is a chart showing correlation between Brookfield viscosities in cps at 30 rpm and wt % dispersant for a 55% wt

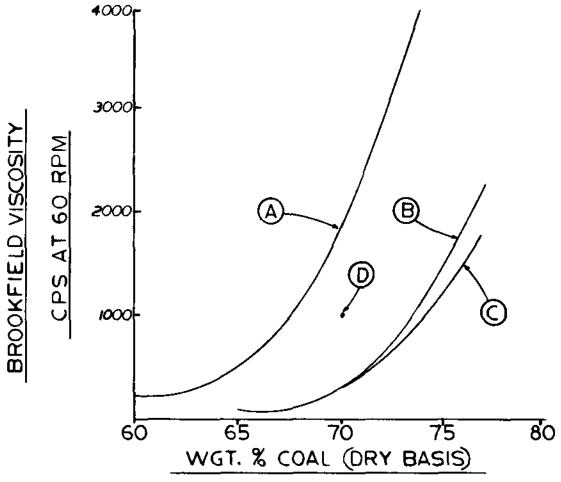


FIG. 2. Alfred formula consist coal/water slurry viscosities (30).

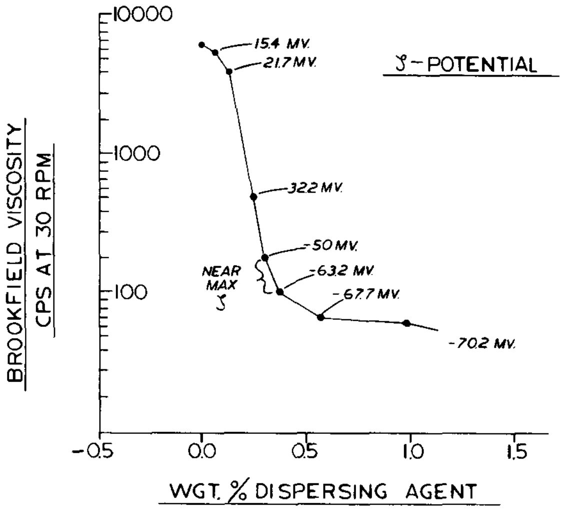


FIG. 3. Correlation of viscosity, zeta potential and amount of dispersing agent in 55% wt coal/water slurry (30).

coal/water slurry. The respective zeta potentials in mV are listed for various dispersant concentrations. It is known that increased zeta potentials raise the dispersion stability. Thus, it is evident that in order to obtain a near maximum zeta potential, a dispersant concentration of 0.5% wt is required. Similarly, Figure 4 is a chart showing the correlation between Brookfield viscosities measured with a T spindle and wt % dispersant for a 70% wt coal/water slurry using calcium lignosulfonate as the dispersant.

The stability of coal/water slurries may be further improved by addition of a stabilizer and conversion of the slurry to a Bingham fluid. For example, settling may be significantly delayed by a 3% solution of hydroxypropylated corn starch (31). Braun et al. (35) have developed improved aqueous slurry compositions with a higher percentage of coal, which can be more readily transported, having present therein up to ca. 10% wt on solids a water-soluble polymer from the group consisting of hydroxyethyl cellulose, the quaternary nitrogen-substituted cellulose ethers, xanthan guar gum and carboxymethyl hydroxypropyl guar gum. Likewise, in our laboratory a system was developed for effective coal/water dispersions of dispersant A-23 with stabilizer CW-11. To illustrate its

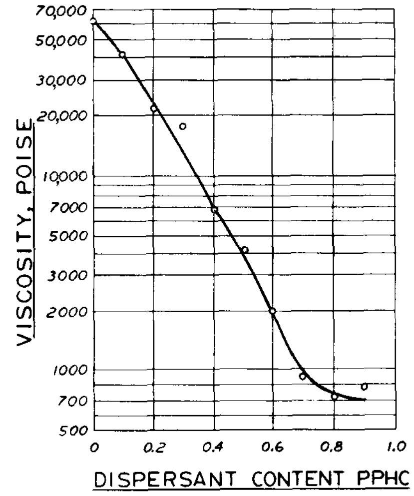


FIG. 4. Effect of dispersant content on T viscosity of 70% wt slurry of Kentucky coal in water dispersant is Norlig II. (*PPHC parts per hundred of mesh coal) (31).

performance characteristics, Figure 5 shows the effect of dispersant concentration on the viscosity of the slurry in the presence of the stabilizer.

Marlow and Rowell (36) have studied the rheology of an Atlantic Research Corporation coal/water slurry containing 65% bimodal washed Kentucky coal, 1.05% hydroxypropylated corn starch (Hamaco 267) and 0.035% biocide (formaldehyde) with a low shear capillary viscometer. The true shear rate as a function of shear stress is shown in Figure 6 for several temperatures: 25, 37, 50 and 65 C. At all temperatures studied, good straight lines are obtained so that the true slurry viscosity could be calculated from the slope at each temperature. These viscosities are 53, 34, 24 and 20 poises for this temperature range. All straight lines

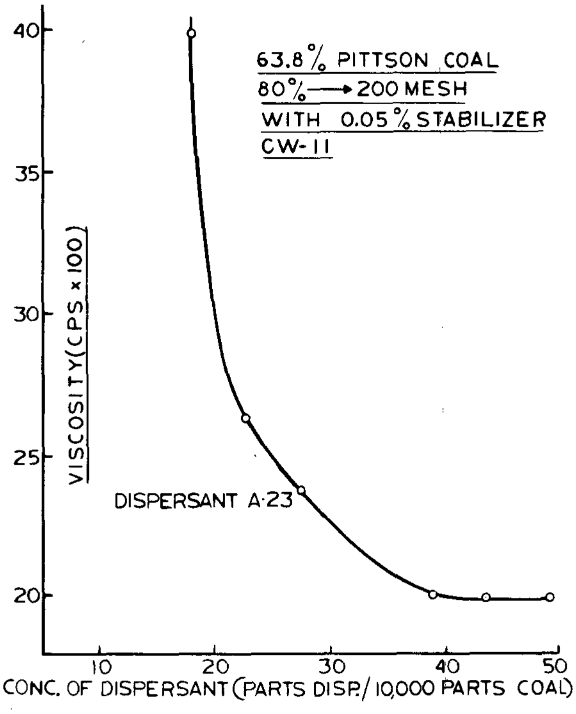


FIG. 5. Coal/water slurry.

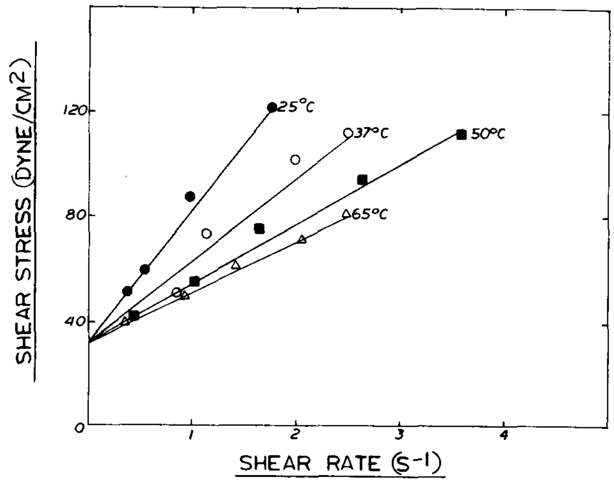


FIG. 6. True shear rate vs shear stress for ARC coal/water slurry at 25, 37, 50 and 65 C (36).

extrapolate to a common intercept at 32 dyne/cm^2, the Bingham yield stress. The activation energy is calculated from the slope in a plot of the logarithm of viscosity (poise) vs the reciprocal of the Kelvin temperature as shown in Figure 7, which amounts to 5.03 kcal/mol. This activation energy for viscous flow in oil of 5.03 kcal/mol is large compared to normal solvents, which have a value of ca. 0.1 kcal/mol. The large activation energy for flow and the constant yield stress independent of temperature suggest significant interparticle forces. Thus, it is concluded that a desirable coal/water dispersion is a loosely flocculated network that yields readily to flow.

It is worth noting that Little (37) recently announced a liquid carbon dioxide/coal slurry process for pipeline transportation for areas of water shortage to replace coal/water slurries.

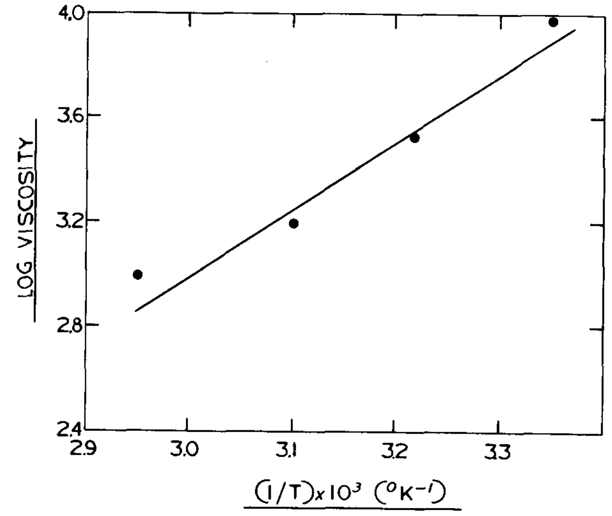


FIG. 7. Log viscosity (poise) vs reciprocal Kelvin temperature (36).

Coal-Oil Dispersions

Coal-in-oil dispersions are useful for pipeline and tank-car transportation and can be burned directly in oil furnaces without modification, and are a basic step in coal liquefaction processes. Extensive research has been carried out in the USA and Japan to ensure that the more economical coal/oil mixtures (COM) for the partial substitution of heavy fuel oils in boilers and furnaces have acceptable pumping, storage and burning characteristics. The objective is to prepare a stable loosely dispersed network of coal in no. 6 fuel oil with structural support and fluidity controlled by interparticle forces. Thus, the role of dispersants in COM stabilization, similar to that previously discussed in coal/water slurries, is to control these interparticle forces. The following experimental methods are being used to study the stabilization of COM by various dispersants: viscosity (38), rod penetration (39), sedimentation with pycnometer (40, 41), solvent extraction (42, 43) and microelectrophoresis (44, 45). In addition, Naka et al. (39) and Cherry (46) have developed the electric current measurement method, which enables one to forecast immediately after preparation the stability of COM after long-term high temperature storage.

The method to determine the stability of COM with a Brookfield helipath viscometer is illustrated in Figure 8 (38) and by rod penetration in Figure 9 (39). The apparatus for measuring COM sedimentation comprises a thermostated jacketed column of 50 cm height and inner diameter of 20 mm (40). The experiments are performed at 50 C and the stability is assessed from intermittent pycnometric density measurements of the effluent. The stability is expressed in terms of the product t_d X SR of sedimentation ratios SR and drain time ratios t_d, where SR is the ratio of the wt % coal in stabilized COM vs the wt % coal in unstabilized COM and t_d is the time required to drain a column containing the stabilized COM vs the time required to drain the control. Dispersants with a low value of t_d X

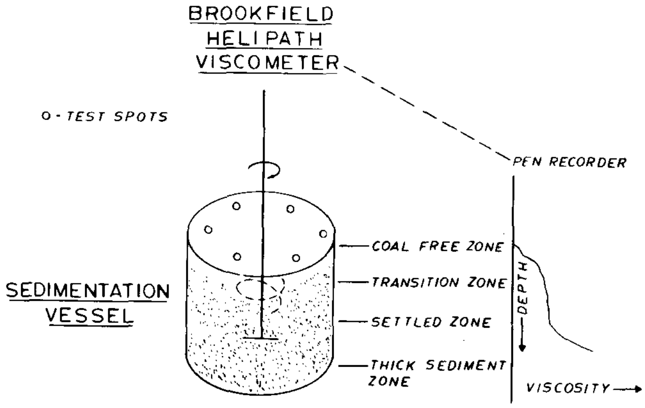


FIG. 8. Brookfield helipath viscometer for stability measurements (38).

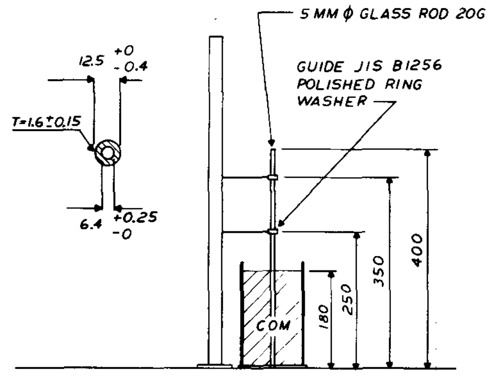


FIG. 9. Rod penetration test equipment (39).

SR signify an effective COM, and vice versa. In the electric current method (39, 46) as shown in Figures 10 and 11, a small voltage of 5–10 V is applied to the COM and the current flowing through the COM is measured. The differcence d1A = 1A – 1Ac between 1A current passing through COM containing an additive and 1Ao without an additive is a measure of COM stability. Thus, if d1A ⩾ 0 the additive is ineffective, and if d1A ⩽ 0 the additive is effective.

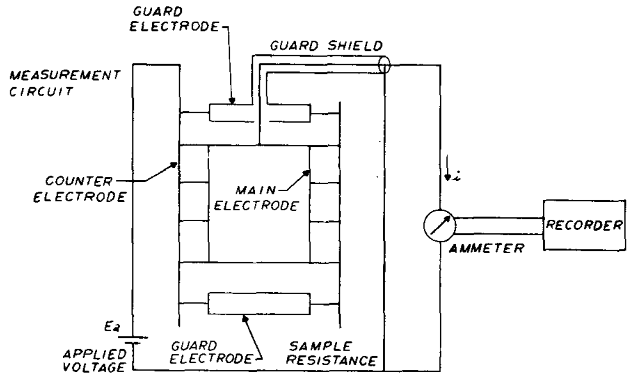


FIG. 10. Electric current method: measurement circuit diagram (39).

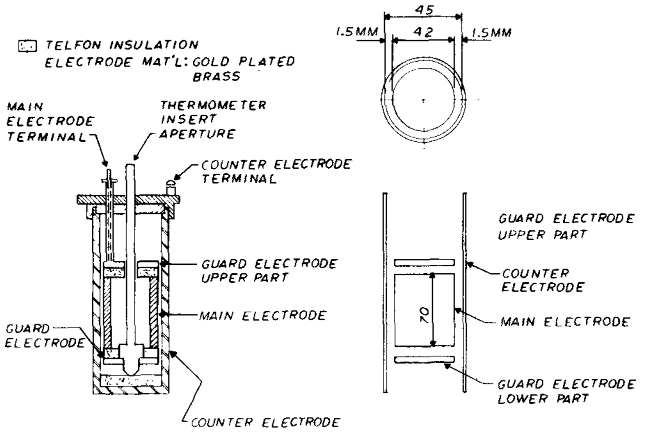


FIG. 11. Electric current method: electrode construction (39).

Copious literature already exists on COM stabilizers (47). Table IV originates from a Japanese source covering a broad spectrum of stabilizers (48). A more quantitative assessment of dispersants for COM is shown in Tables V and VI (40, 49), which indicate that cationic surfactants as a class are the most effective COM dispersants and within

TABLE IV

Types of Stabilizing Agents for COM (48)

Type	Functional group	Type
Anionic surfactants	Compounds having $-SO_3^-$ radical or $-OSO_4^-$ radical	Alkylbenzenesulfonic acid type Petroleum sulfonic acid type Alpha sulfonic fatty acid ester type Sulfosuccinate type Olefinesulfonic acid type
	Compounds having $-SO_3^-$ radical or 2 or more $-OSO_4^-$ radicals	Substituted aromatic sulfonic acid condensate Alkyldiphenylether disulfonic acid type, styrene-sulfonic acid polymer
	Compounds having $-COO^-$ radical	Soap type Monocarboxylic acid type Polycarboxylic acid type
	Compounds having $-OP(OM_2)$ radical	Phosphoric acid ester type
Nonionic surfactants	Compounds having (EO) or $(PO)_m(EO)_n$ radicals	$R-N(EO)_nH$ $RO(EO)_nH$ $(BO)_l(PO)_m(EO)_n$ Polyether polyol (MW: 1,000–100,000) Compounds having more than four EO radicals
	Derivatives having (EO) or $(PO)_m(EO)_n$ radicals	Sulfate and/or phosphate of polyether Formalin condensates of polyether Peroxide-crosslinked compounds of polyether Polycarboxilic halide-crosslinked compounds of polyether Epoxy/aldehyde-crosslinked compounds of polyether AO•EO copolymers Polyalkylenepolyamine
Cationic surfactants	Quaternary ammonium salt	Monoalkyl type Dialkyl type
	Fatty-amine derivatives	Mono/polyamine derivatives Amine having amide radical Amine having ether radical
Others		Vinylpolymers Polysaccharides Low alkyl alcohol

TABLE V

List of Surfactants (49)[a]

Sample	Structure
	Anionic surfactants
Alipal CO436	NH_4 + salt of sulfate ester of alkylphenoxypolyol
Span 60	Sorbitan monostearate
Span 40	Sorbitan monopalmitate
Blancol N	Sodium salt of condensed naphthalene sulfonic acid
Deriphat 170C	Sodium salt of lauryl myristyl-β-amino propionic acid
	Cationic surfactants
CTAB	$CH_3(CH_2)_{15}N(CH_3)_3Br$
CTAC	$CH_3(CH_2)_{15}N(CH_3)_3Cl$
CTAS	Cetyl trimethyl ammonium stearate
Triton X-400	Benzylalkonium chloride
Ethomeen C-15	$CH_3(CH_2)_{14}N(C_2H_4O)mH(C_2H_4O)nH$
Ethomeen C-20	$CH_3(CH_2)_{19}N(C_2H_4O)mH(C_2H_4O)nH$
Atlas G-271	N-soya-N-ethyl morpholinium ethosulfate
	Nonionic surfactants
Merpol SH	$CH_3(CH_2)_{12}(OC_2H_4)_8OH$
Merpol HC	$CH_3(CH_2)_7CH{=}CH(CH_2)_8(OC_2H_4)_{20}OH$
Brij 78	Polyoxyethylene (20) oleyl ether
Tween 20	Polysorbate 20 polyoxyethylene (20) sorbitan monolaurate
Tetronic 1104	Polyol

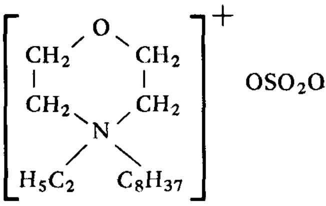
[a]The surfactants listed above are trademarks of the following companies: Ethomeen-Armak, Inc.; Tetronic-BASF Wyandotte Corp.; Alipal and Blancol-GAF Corp.; Deriphat-Henkel Corp.; Span, Tween, Atlas and Brij-ICI America, Inc.; Triton-Rohm and Haas Co.; Merpol-E.I. DuPont de Nemours Co.

TABLE VI

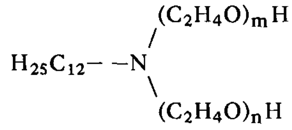
Results of Surfactant Screening (49)

Sample	SR	t_d	$t_d \times SR$
	Anionics		
Alipal CO-436	.696	.66	.459
Span 60	.822	.72	.529
Span 40	.832	.76	.632
Blancol N	.976	.92	.898
Deriphat 170C	.888	.86	.764
	Cationics		
CTAB	.794	.70	.556
CTAC	.754	.64	.483
CTAS	.605	.62	.375
Triton X-400	.721	.69	.498
Ethomeen C-15	.700	.50	.350
Ethomeen C-20	.583	.48	.280
Atlas G-271	.621	.44	.273
	Nonionics		
Merpol SH	.765	.60	.459
Merpol HC	.790	.64	.506
Brij 78	.832	.77	.641
Tween 20	.917	.88	.807
Tetronic 1104	.655	.70	.459

that class, Atlas G-271, Ethomeen C-20 and Ethomeen C-15 are the most effective ones. Their structural formulas follow.

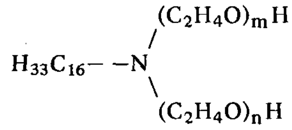


Atlas G-271: N-soya-N-ethyl morpholinium ethosulfate



$$H_{25}C_{12}{-}N\begin{cases}(C_2H_4O)_mH\\(C_2H_4O)_nH\end{cases}$$

Ethomeen C-15: m + n = 5



$$H_{33}C_{16}{-}N\begin{cases}(C_2H_4O)_mH\\(C_2H_4O)_nH\end{cases}$$

Ethomeen C-20: m + n = 10

In addition, block copolymers of polyoxypropylene-polyoxyethylene (50–52), polyol condensates (53), imidazolines (54–56), alkylene oxide adducts of amines (57, 61), carboxylic acids and phenols (61), reaction products of polycyclic, polycarboxylic acids with a base (58), sorbitol derivatives (59) and dialkylsulfosuccinates (60) have been claimed to be effective COM dispersants.

The interaction between surfactant stabilizers and coal surfaces should be examined. Adams-Viola, Botsaris and Glazman (43) have investigated the hydrophilic/lyophilic nature of coal surfaces, i.e., the philicity, by selective wetting in oil/water systems. Coals were classified as hydrophilic or lyophilic, respectively, by investigating their agglomeration in a mixture of equal volumes of kerosene and water. The authors concluded that the stabilizing effect of a surfactant is a function of the nature of the coal—in particular, its surface philicity.

Kosman and Rowell (42) have used a different approach to characterize the philicity of a surface. They examined the interaction of a surfactant with bituminous coal by correlating the removal of the adsorbed species in solvent extraction with the electrophilic and nucleophilic properties of the desorbent or extractant. The electrophilic/nucleophilic approach is based on the Lewis concept that a base is an electron-pair donor and an acid is an electron-pair acceptor. The electrophilic properties are expressed in terms of an empirical parameter, the acceptor number AN, whereas the nucleophilic properties are in terms of the donor number DN.

Kosman and Rowell (42) selected the cationic surfactant, Atlas G-271, N-soya-N-ethyl morpholinium ethosulfate for their investigation, which has been shown in Table VI to be a very effective stabilizer for COM (49). Analysis of the coal phase separated from a COM by centrifugation showed that the surfactant was quantitatively associated with coal. Subsequently, the removal of the surfactant from the coal phase was studied by solvent extraction and the results are illustrated in Figure 12. It is evident that the extraction efficiency increases with the AN number of the solvent and that the AN number must exceed 23 in order to remove Atlas G-271 from the coal surface, which suggests that the particular coal used has an AN philicity of 23. In addition, it was found that the particular coal used has a DN philicity of 19–20 kcal/mol irrespec-

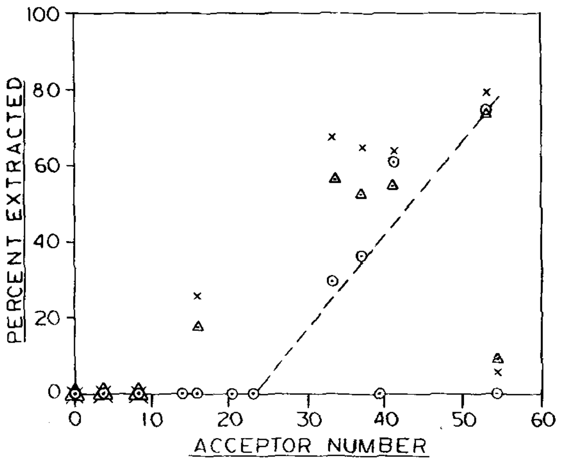


FIG. 12. Extraction of Atlas G-271 from coal centrifuged from aqueous and nonaqueous slurries, mineral oil slurry, distilled water slurry, sea water (ASTM) slurry. Reprinted from ref. 42, p. 252, courtesy of Elsevier Publishing Company.

tive of extractant used. An upper-limit coordinate bound energy of 4.6 kcal/mol derived from these data indicates that the binding is by physical adsorption.

In Figure 13, three possible orientations of Atlas G-271 on the coal surface are examined in terms of specific site binding. Only an ion-paired unit would be the likely configuration in nonaqueous media. The three types of sites on the coal surface shown in Figure 13 are neutral (0), nucleophilic (N) and electrophilic (E). The AN/DN properties of the extracting solvent are shown under the heading substitution. Orientation 1 is ruled out, because the AN/DN properties for effective removal do not fit the experimental results. Orientation 2 illustrates binding between a nucleophilic site and electrophilicly oriented ion pair, whereas orientation 2 shows binding between an electrophilic coal site and a nucleophilicly oriented ion pair. Although both orientations 2 and 3 are possible for an ion-paired surfactant, the AN/DN properties of effective removal favor orientation 2. It follows that the coal surface must be primarily nucleophilic in character, which required a cationic surfactant for COM stabilization. This configuration of an ion-paired unit with the polar head group oriented toward the electron-donating sites on the coal matrix and the hydrocarbon tail extending outwards, also conform with the concept of network stabilization in COM cited above. Microelectrophoretic studies of both of the coal particles and of the coal particles coated with adsorbed Atlas G-271 in media of low dielectric constant demonstrated that the particles were uncharged in direct confirmation of the ion-pair mechanism postulated above.

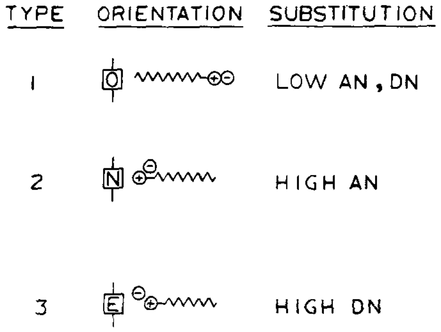


FIG. 13. Possible orientations of adsorbed cationic surfactant on a neutral coal site (O), nucleophilic coal site (N) and electrophilic coal site (E). Reprinted from ref. 42, p. 251, courtesy of Elsevier Publishing Company.

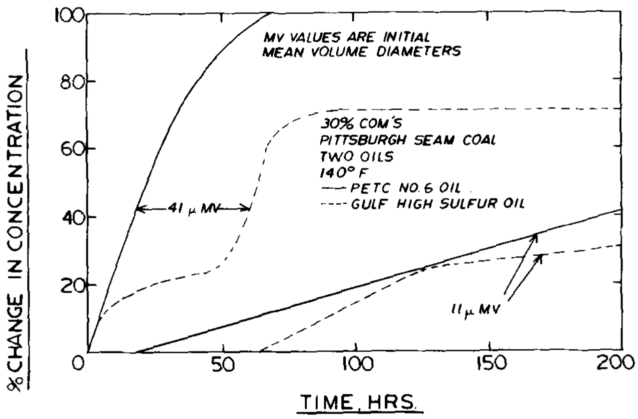


FIG. 14. The effect of coal particle size on settling behavior of COM (62). Percentage decrease in concentration as a function of time.

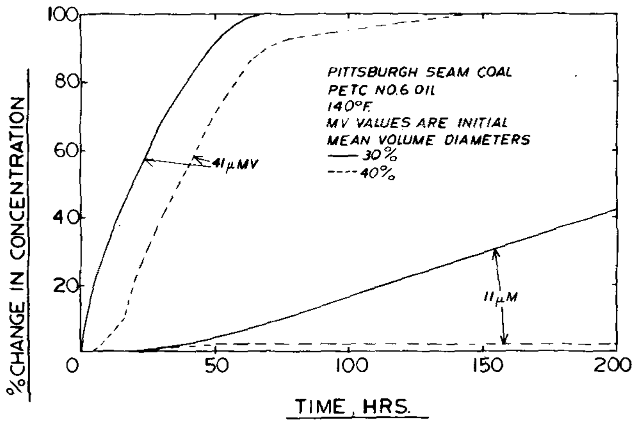


FIG. 15. The effect of coal particle size on settling behavior of COM (62). Percentage decrease in concentration as a function of time.

Extensive research has been carried out on the effect of coal particle size (62–69) and rheology (41, 70–76) on coal/oil slurries. As shown in Figures 14 and 15, settling characteristics showed a significant dependence on particle size (62), however, with 30% wt COM in no. 6 fuel oil or Gulf high sulfur oil the stabilizing effects by reduction in particle size seemed to level off below 10 μm. Higher viscosity Gulf high sulfur oil raises the viscosity of 30% COM nearly ten times compared to the PETC oil no. 6, which is reflected in the pattern of settling. Aiken and Ekmann (72) observed step-changes in the settling curves of 30% COM in Gulf high sulfur oil (see Fig. 14) which, according to these authors, support the arguments for structure formation in COM. The reduced settling rates that occur with increased concentration are attributed to a different cause. COM viscosity increases less than twice when the concentration is raised to 40% from 30% in the same oil, yet the effectiveness of this change is as significant as that caused by the more viscous oil. The effect is comparatively small with the 41 μm slurry (see Fig. 15), but is much greater with the 11 μm slurry. This is probably due to the comparative increases in number of particles when the concentration is increased. Thus, for an equal increase in weight percent, the increase in the number of particles is greater when the particle size is smaller. This causes the effects of concentration increase to be comparatively large for very fine COM.

Let us now review some rheological phenomena. As shown in Figure 16 (70), the viscosity increases with increasing coal concentration, but decreases with increasing shear. Furthermore, it is evident that the viscosity of lignite no. 2 with a volatility of 46% increases more rapidly than th viscosity of a bituminous coal no. 4 with a volatility of only 14%. Therefore, Rejek and Franke (70) suggest that, to avoid undue increase in viscosity, the coal concentration for pipeline transportation should not exceed 50% wt with lignite and 65% with bituminous coal within a temperature range of 50–80 C. Papachristodoulou and Trass (71) have studied the rheological properties of an ultrafine COM. They have identified COM as a Newtonian fluid at coal concentrations up to 30% wt and as a Bingham plastic at higher values. The COM yield stress increases with increasing coal concentration, decreasing temperature, and increasing time. The increase in yield stress over a period of several days for COM consisting of 60% coal in no. 2 fuel oil is illustrated in Figure 17. This increase in yield stress with time suggests again the formation of a network.

COM can be further stabilized by a gelling agent (77, 78). For example, a combination of a suitable surfactant with a gelling grade clay such as colloidal attapulgite of Wyoming bentonite increased the COM stability (77). This stabilizer imparts high viscosity under low shear when the slurry is static, while exhibiting low viscosity under high shear to facilitate pumping, supporting the concept of network stabilization in COM.

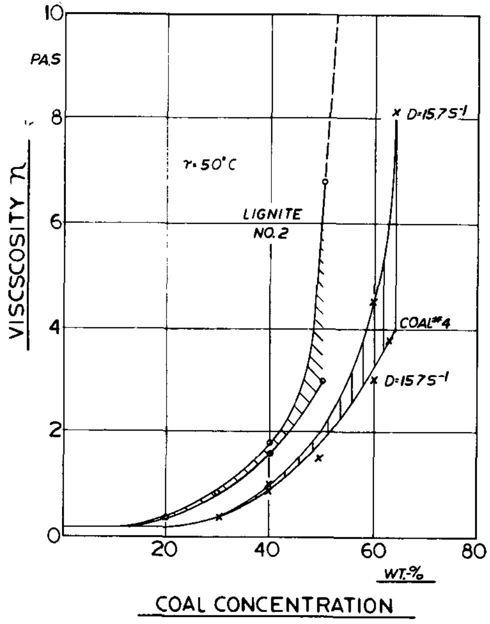


FIG. 16. The effect of coal concentration on COM (70).

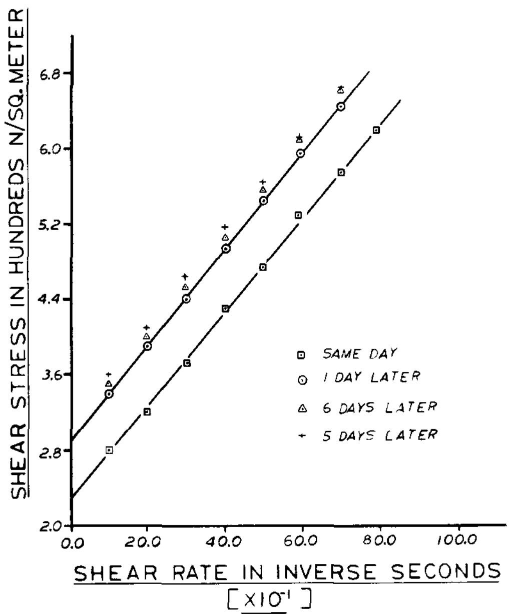
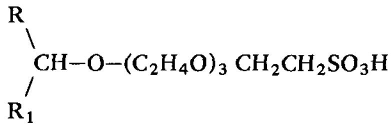


FIG. 17. Effect of storage time on rheological behavior of 60% wt coal in no. 2 fuel oil (71).

Demineralization of Coal

Surfactants are also used in the pretreatment of coal in order to remove inorganic (ashing) ingredients and modifying the coal to render it more amenable to further treatment, for example, liquefaction at considerably lower temperature, etc. In coal/water slurries, elimination of ash reduces energy consumption and abrasiveness. Numerous processes for removing mineral matter from coal are cited among the references (26, 27, 79–88). For example, Liotta (79) has developed a method for comminuting and simultaneously removing mineral matter from coal by first treating the coal with a quaternary base solution (R_4MOR'), such as tetrabutylammonium hydroxide, followed by physical separation of the mineral matter by any conventional separation technique based on the density differences of the two materials. Clayfield et al. (80) have developed a process for the agglomeration of coal fines characterized by the staged addition of an aqueous emulsion containing 0.1% wt of surfactant of an oil fraction to an aqueous slurry of the fines. In this process the ash content is reduced from 35% to 7% wt. Suitable surfactants are sodium C_8–C_{18} secondary alkyl sulfates or sodium salt of


$$\begin{matrix} R \\ \quad\diagdown \\ & CH{-}O{-}(C_2H_4O)_3\,CH_2CH_2SO_3H \\ \quad\diagup \\ R_1 \end{matrix}$$

where R and R_1 are alkyl radicals with a total of 5 carbon atoms.

Flotation of coal with latex emulsion of hydrocarbon may be used to reduce the ash content of coal (26, 27). This method uses a latex emulsion prepared from a hydrocarbon oil with a hydrophobic w/o emulsifier and a hydrophilic surfactant. This process gives high yields of low ash coal without the use of expensive polymers.

Freeze Conditioning Agents

Methods have been developed for reducing the strength of ice to facilitate unloading of coal from railroad cars or, in other words, frozen coal can be easily broken apart without the use of heated sheds. As an effective freeze-conditioning agent (FCA), a composition of a water-soluble polyhydroxy compound or monoalkylether thereof, such as ethylene glycol or the monobutyl ether of ethylene glycol, and a watersoluble organic compound such as sodium acetate or polyacrylamide has been claimed (89). In our laboratory, two nonoil-based (90) FCA, Icephobe CG (91) and GL (92), and a liquid hydrocarbon analogue, Icephobe HF (93) have been developed. The former are based on a blend of polyhydric alcohols with anticorrosive agents and the latter is a blend of hydrocarbons.

Side-Car Release Agents

A very serious problem arises when coal freezes to the sides of the hopper cars, thereby preventing easy unloading and tying up railroad equipment. The adhesion of coal to steel or aluminum is due to water vapor condensing on the walls and diluting the freeze-conditioning agent. The process continues with time until the coal reaches final destination resulting in a 1–2 ft frozen coal layer adhering to the metals. Kekish and Kugel (94) have developed a side-car release agent (SRA) comprising a coating composition of 55–97% by wt of a fuel oil and 3–45% by wt of a hydrocarbon oil-soluble surfactant with an HLB value of 1–8. In our laboratory a multicomponent noncorrosive SRA has been developed, Icephobe HS, which is based on hydrocarbons (95).

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Surface Activity of Separated Phases of the Surfactant/Water/Corn Oil System

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ABSTRACT

Aqueous solutions of octyl phenoxy polyethoxy ethanol (Triton X-114) show phase separation on standing and also in the presence of corn oil. The surface tension of varying concentrations of the upper phase of these systems decreases markedly at lower concentrations, tending to become constant at higher concentrations. The surface activity of this phase as observed from surface tension/concentration curves may be greater, less than or about the same as that of the corresponding upper phase concentration of the control which is a surfactant solution without the oil. Results of this study indicate that the surface activity of the upper phase of Triton X-114 solutions is not affected so much by the solubilization of corn oil but by the limit to which solubilization has occurred. The surface activity of this phase is much less than that of the lower phase of corresponding systems. However, the surface activity of the lower phase is not influenced by the solubilizate or solubilization of the oil.

INTRODUCTION

When a solution of nonionic surfactant is heated to a particular temperature, it suddenly becomes cloudy. This occurs within a narrow temperature range and is termed the cloud point. Above the cloud point, there is a tendency for the solution to separate into two phases. This is believed to be associated with the solubility of nonionic surfactants, which increases by virtue of the power of the ether oxygen to hydrate (1, 2). Hydration is sensitive to temperature. Elevated temperature causes dehydration. Consequently, nonionic surfactants of the polyoxyethylene type become markedly less soluble at elevated temperature, the surfactant solution turns turbid and eventually phases separate out.

Debye (3) has shown that the micellar weight of a nonionic surfactant increases rapidly when the temperature of the solution approaches the cloud point. It will appear, therefore, that the micelle becomes much larger with rise in temperature and finally separates from the water phase. This means that the clouding phenomenon and the subsequent phase separation takes place as a result of the formation of very large aggregates. This is yet another interpretation of the mechanism of phase separation.

The cloud point of aqueous solutions of nonionic surfactants may be affected by the incorporation of coexisting substances. It would seem that a coexisting substance may affect the cloud point of a nonionic surfactant in one of two ways, either by changing the structure of the micelle by penetration of the coexisting substance or by dissolving in the water phase and thereby changing the environment of the micelle (4).

Two-phase liquid systems of Triton X-114 and corn oil as a solubilizate have not been studied previously, as evidenced by the lack of references in the literature. The purpose of the present investigation is to examine the surface activity of the phases resulting from the phase separation of Triton X-114 solutions to which corn oil has been added. It represents a logical sequence to the attempts made previously to solubilize corn oil with various surfactants (5, 6). In the study of the solubilization of corn oil with Triton X-114 solutions (6), it was found that the solubilization of this oil did not follow the usual behavior of most other solubilized systems in that the amount of solubilizate taken into the micelle did not increase with surfactant concentration; much higher concentrations than normal were required to solubilize the oil and the process took several days instead of the usual, almost spontaneous, taking in of the solubilizate into the micelles.

EXPERIMENTAL

Materials

Corn oil (Mazola, Best Foods Div., CPC International Inc., NJ) of commercial grade was used. The surfactant employed was octyl phenoxy polyethoxy ethanol (marketed as Triton X-114 by Rohm and Haas, Philadelphia, PA).