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Adsorption of Polyoxyethylated Detergents on Quartz

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Detergents prepared by condensation of ethylene oxide with an alkylphenol have attained widespread industrial usage. Because the mole ratio of ethylene oxide to phenol can be varied continuously above a value of 1, detergents with a wide range of properties may be prepared readily. Detergents of this type appear promising as additives to water injected into petroleum-producing formations to stimulate petroleum production. They have been investigated extensively for this specific application and for more general applications (*3, 4, 8–10*). The surface activities (*3, 8*), interfacial activities (*4, 8*), and critical micelle concentrations (*7*) of these detergents have been investigated recently.

Because of the extremely large surface areas of petroleum-producing formations, adsorption of detergents may cause their use to be economically prohibited. However, application of the chromatographic theory (*2, 11*) to detergent movement in such reservoirs indicates that adsorption may not be an insurmountable obstacle. The basic data for calculations according to the chromatographic theory, and of many other surface functions (*1*), are obtained as adsorption isotherms.

A comparative study of the adsorption of Igepal CO-710 on sand was made recently in an investigation of the mechanism of adsorption (*6*). No general study of the adsorption characteristics of series of polyoxyethylated detergents has been made, although the data would be of considerable practical value. The adsorption of six members of series based on nonylphenol and of three members of the octylphenol series has been investigated with a fine quartz powder. The data afford comparisons of the effects of composition on adsorption and allow generalizations of the behavior of similar detergents.

MATERIALS

The quartz powders were sized carefully by sedimentation from a crushed sample of commercial quartz. They were cleaned with hot chromic acid, washed extensively with deionized water, rinsed with reagent grade acetone, and dried at 110° C. The quartz powder used in most of the experiments contained particles ranging from about 0.5 to 4 microns and averaging 2 to 3 microns in diameter. A coarser powder used for a few of the experiments ranged from 3 to 13 microns and averaged about 8 microns in diameter. The surface areas of the powders were 3.9×10^4 and 1.1×10^4 sq. cm. per gram, respectively, as determined by the B.E.T. nitrogen-adsorption method.

The detergents were of the polyoxyethylated alkylphenol type and represented homologous series based on nonyl- and octylphenol in which the hydrophilic polyoxyethylene chains varied in length. Two of these series were described previously and were designated "Series II" and "Series III", respectively (*3*). Series II comprises Igepal CO-710 homologs (General Aniline and Film Corp., New York) and series III, Triton X-100 homologs (Rohm and Haas Co., Philadelphia). The various detergents are designated "NR" or "OR" to indicate nonyl- or octylphenol, and by a numeral to indicate mole ratio of ethylene oxide to phenol.

Thus, NR-20 is a detergent composed of 1 mole of nonylphenol and an average of 20 moles of ethylene oxide. Two of the detergents, NR-7.9 and NR-11.5, were molecularly distilled samples similar to those described by Mayhew

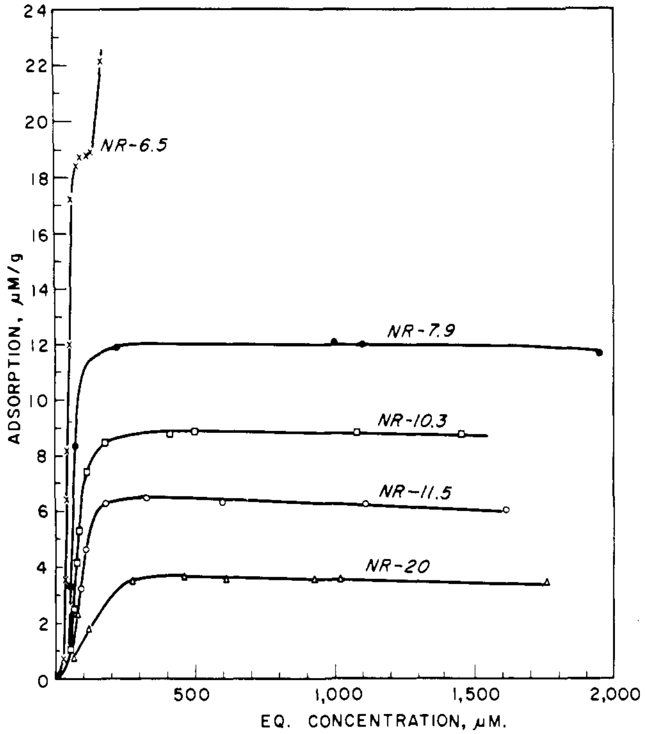

Figure 1. Adsorption of Igepal CO-710 homologs on quartz powder (molar basis)

(*10*). One member of the Surfonic (Jefferson Chemical Co., New York) series, based on nonylphenol, also was studied. Mole ratios of ethylene oxide to phenol were calculated from absorbance values at 276 mμ.

Water was prepared by distilling deionized water in a conductivity still. The chemicals used were analytical reagent grade.

EXPERIMENTAL METHODS

Measured volumes of solutions of known concentrations were shaken with weighed amounts of quartz on a "wrist-action" shaker for several hours. The vials containing the solutions and quartz samples were centrifuged for 30 minutes at a centrifugal force of 1700 times gravity. Then a portion was carefully pipetted from the interior of the liquid phase, diluted if necessary, and centrifuged again. The centrifuged liquid then was analyzed and the amount of adsorption was calculated from the observed decrease in concentration. Concentrations generally were determined by measurement of the absorbance of ultraviolet light with a Beckman Model DU spectrophotometer. Determinations were made in duplicate or triplicate. In the usual spectrophotometric method, absorbance was measured at 276 mμ, a wave length of maximum absorbance for these detergents, and corrected for residual suspended material by subtracting the absorbance at 300 mμ. This correction averaged less than 2% of the total absorbance. The repeated centrifuging removed almost all of the quartz from suspension and generally made it unnecessary to apply the two-wave length method of calculation (*6*).

RESULTS

The adsorption isotherms of the Igepal homologs are plotted on a molar basis in Figure 1. Average results of duplicate determinations are indicated. Experimental points have been omitted at the lower concentrations to avoid confusion. The maximum amounts of adsorption decrease rapidly with increasing mole ratio of ethylene oxide. The isotherms are nearly linear at lower concentrations and the slopes of these linear portions decrease with increasing mole ratio. The concentrations at which the isotherms begin to deviate markedly from linearity, as the maxima in adsorption are approached, increase with mole ratio of ethylene oxide.

The adsorption of three of the Triton homologs is illustrated in Figure 2. The average results of duplicate determinations are indicated. The maxima in adsorption of these detergents are comparable to those of the Igepal series which they resemble in hydrophilic-lipophilic balance. However, the maxima are reached only at considerably higher concentrations with the Triton X-100 homologs. The location of the concentrations at which adsorption ceases to vary linearly with concentration is difficult. However, extrapolation of the two nearly linear portions of an isotherm to their intersection appears to be a reasonable method of estimation. This point of intersection will be termed the "critical adsorption concentration." Values of this function, maximum adsorption, and slope of the initial portion of the isotherm are summarized in Table I.

The desorption isotherms of OR-12 and of a member of the Surfonic series (NR-11.5) were determined in a study of the reversibility of adsorption of such detergents. The adsorption and desorption isotherms of these detergents are shown in Figure 3.

The amounts of OR-12 adsorbed from solution (on a surface area basis) by the two powders agreed within the experimental error of the adsorption and surface area determinations.

The surface properties of these detergents are affected by electrolyte concentration (*7*), and much of the water used in waterflooding oil fields is highly saline. Because these detergents are promising as additives for such flood water, the adsorption of NR-20 and OR-17 from 1*N* sodium chloride solutions was investigated.

The adsorption isotherm of NR-20 in 1*N* sodium chloride solutions is shown in Figure 4. Similar effects of salt concentration on the adsorption of OR-17 were observed. The values of maximum adsorption, slope of linear portion of isotherm, and critical adsorption concentration are summarized in Table I. The maximum extents of adsorption were increased about 25% in the salt solutions, while adsorption at lower concentrations was increased sharply; the slopes of the linear portions of the isotherms were about tripled.

DISCUSSION

The decreased adsorption resulting from increasing the content of hydrophilic polyoxyethylene in the molecule is

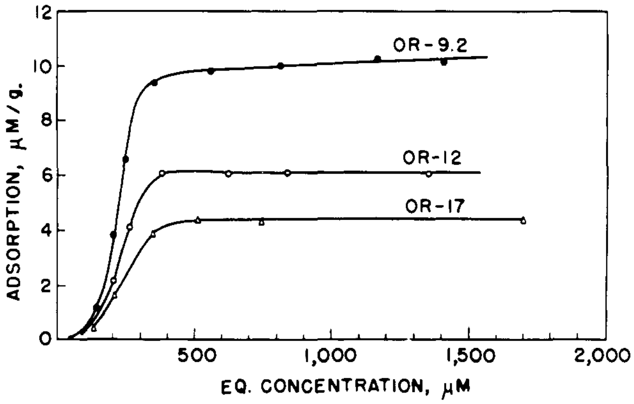

Figure 2. Adsorption of Triton X-100 homologs on quartz powder (molar basis)

Table 1. Adsorption Properties of Detergents

Detergent	Solvent	Max. Adsorption		Initial Slope,	Critical Adsorption Concn.	
		μmole/gram	$10^4 \times$ gram/gram	(μmole)/(Gram $\times$ Cμmole)	μmole	P.p.m.
NR- 6.5	Water	18.8	95.7	0.47	70	35
NR- 7.9[a]	Water	12.0	68.0	0.27	90	50
NR-10.3	Water	8.7	58.5	0.14	110	75
NR-11.5[b]	Water	6.7	48.6	0.15	90	65
NR-11.5[a]	Water	6.5	47.2	0.08	130	95
NR-20	Water	3.6	39.0	0.02	250	270
OR- 9.7	Water	10.0	63.4	0.07	290	185
OR-12	Water	6.1	45.9	0.03	330	250
OR-17	Water	4.4	42.9	0.02	380	370
NR-20	1*N* NaCl	4.3	46.6	0.06	80	85
OR-17	1*N* NaCl	5.8	56.5	0.045	180	175

[a] Molecularly distilled sample.
[b] Surfonic series.

to be expected because the solubility of the detergent in water is increased accordingly. The decreased adsorption parallels generally the decreased surface activity at the air-water interface (*3*, *8*), and reflects a departure from the optimum hydrophilic-lipophilic balance of the molecules. Economically, there would appear to be little reason for choosing a detergent of these series having a mole ratio of over 12 or 14 if it is to be used in fresh water solutions having concentrations above 400 p.p.m. The adsorption on a weight basis, by which detergents are marketed, ceases to decrease at about this mole ratio. Furthermore, the general detersive ability and the efficiency of such detergents in displacing crude oil from sand surfaces are lower at the higher mole ratios of ethylene oxide (*3*, *8*).

The two series have comparable adsorption maxima at corresponding mole ratios and solubility properties. Other detergents of this type such as the Synthetics (Hercules Powder Co., Wilmington, Del.) series, one of which was used recently in a large-scale field test (*5*), would be expected to behave similarly.

The extent of maximum adsorption is not changed appreciably by the change from nonyl- to octylphenol and may be expressed (within an average deviation of ± 7%) by the equation

$$\Gamma_{\text{max.}} = \frac{250}{R^{1.45}}$$

where $\Gamma_{\text{max.}}$ is expressed in micromoles per gram of quartz and R is the mole ratio of ethylene oxide to octyl- or nonylphenol.

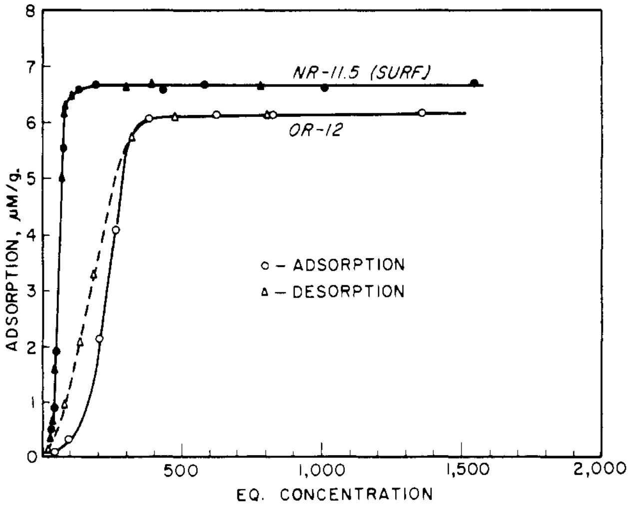

Figure 3. Adsorption and desorption of detergents on quartz powder

Although the maximum adsorption values are comparable between the two series, adsorption of the Triton homologs at lower concentrations is much less than that of the Igepal homologs (Table I). This behavior is parallel to that at the air-water interface (*7*), where it was observed that decreasing the alkyl chain by one methylene unit about doubled the critical micelle concentration. The "critical adsorption concentration" of the Igepal homologs in water may be expressed approximately by the expression

$$\log (\text{CAC}) = 0.037\,R + 1.66$$

This expression is similar to that describing the variation of critical micelle concentrations with R for this series of detergents.

The two molecularly distilled samples (NR-7.9 and NR-11.5) have adsorption characteristics typical of the series they represent, indicating that the width of the chain-length distribution curve does not have a marked effect on the properties of such detergents in this system.

The desorption studies (Figure 3) corroborate the reversibility of adsorption of these detergents and indicate that their movements through porous materials may be predicted from the chromatographic theory. Desorption values of NR-11.5 (Surfonic) are practically identical with adsorption values at corresponding equilibrium concentrations. Desorption values in the lower concentration range with OR-12 are appreciably greater than the corresponding adsorption values, but are equal to them at higher concentrations.

The adsorption isotherms shown above do not exhibit the second increase in adsorption reported previously for

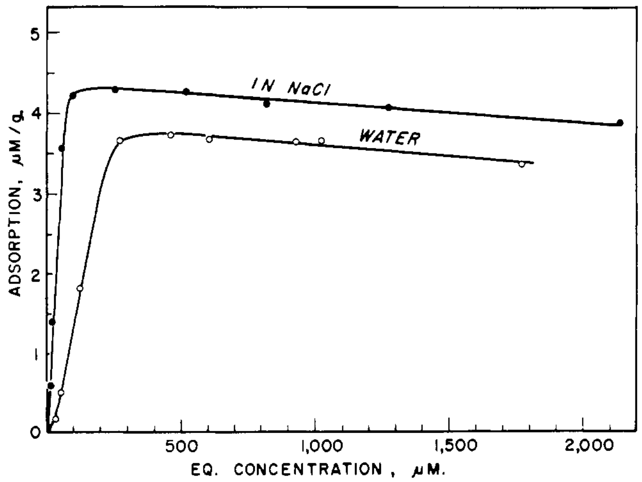

Figure 4. Adsorption of NR-20 on quartz powder from water and salt solution

Igepal CO-710 on sand (*6*) and generally are of the Langmuir type. As a result of more extensive study, it is concluded that the final increase in adsorption reported for this detergent is not valid and is a reflection of the large experimental error caused by the suspension of fine calcite particles identified in the sand sample.

The effect of electrolyte concentration on the adsorption of these detergent series is similar to the effect on the critical micelle concentrations of the Igepals (*7*). The maxima in adsorption are not increased markedly, but they occur at much lower concentrations. High electrolyte concentrations decrease the hydrophilicity of these detergents. Therefore, for comparable results, detergents used in saline water should have a higher ethylene oxide content than those used in fresh water. These results indicate that the detergents could be used effectively in strongly saline water, as well as in fresh water.

ACKNOWLEDGMENT

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Comparison of Brazilian and Colorado Shale Oils

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Lack of uniformity of retorting operations on shales from various localities has made it difficult to separate the effects of retorting from those contributed by the nature of the oil shale. Analyses of oils obtained from Colorado shale by various retorting methods and of oils from a number of countries have been published (*11*). These latter oils in general resulted from commercial retorting, so did not give information as to the range in product composition obtainable by different retorting methods or different operating conditions in the same retort. In the present investigation, oils obtained by retorting Paraiba Valley shale from Brazil in six experimental retorts have been analyzed. Comparison of selected properties with those on a similar series of Colorado oils affords an opportunity to distinguish between the effects of shale composition and retorting conditions.

The content of low-boiling distillate in oils from Colorado or Brazilian shale showed substantial differences, which depended largely on retorting method. The quantity of residuum in an oil from Colorado shale was always greater than in the corresponding oil from Brazilian shale, an indication of an effect of shale composition. The structure of the organic matter in the two shales differs with respect to the nitrogen linkages present, as evidenced by data on the oils produced from the shales. The proportion of nitrogen in the organic matter in Colorado shale that appeared in the oil was substantially higher than for the Brazilian shale. The nitrogen in all the Colorado oils analyzed was concentrated in the higher-boiling fractions, as has been found for other oils, but its boiling range distribution in four of the Brazilian oils was relatively uniform. The sulfur contents did not show an effect of shale composition similar to that observed for nitrogen. When produced under equivalent conditions, the Colorado oils contained more saturated and correspondingly less aromatic hydrocarbons than the Brazilian oils.

EXPERIMENTAL

The analyses discussed were obtained by the Bureau of Mines method (*11*) for the analysis of crude shale oil. The composite fractions indicated in the outline (Figure 1) are designated for ease of discussion as naphtha (fractions 1 to 7), light distillate (fractions 8 to 10), and heavy distillate (fractions 11 to 14). A summary of results pertinent to the present discussion is given in Table I for eight oils from Brazilian (Paraiba Valley) shale and four oils from Colorado shale. Complete analytical data on these oils have been published (*1, 11*).

The Brazilian oils for this work were obtained from experimental operations in six different retorts which may be grouped into three types according to the method of heating used. The Union (*7*) and Gas Combustion (*2*) retorts were internally heated; the entrained solids (*9*) and Fischer assay (*10*) retorts, and for one run the Parry (*6*) retort, were externally heated. The remaining runs on the Parry retort and the Otto (*4*) retort used a combination of these methods of heating. The Union, Gas Combustion, and Otto retorts have lump shale moving countercurrent or transverse to the gas phase. The entrained solids and Parry retorts treat finely ground shale in the entrained state. The Fischer assay retort is a small laboratory unit in which a charge of shale,