Absorption of Dodecylbenzenesulfonate on Earth Sediments

Liquid-Solid Phase Equilibrium

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The adsorption isotherms of sodium dodecylbenzenesulfonate in water on four unconsolidated and three consolidated earth sediments were measured at room temperature; the solution concentration at equilibrium ranged from 1 to 87 mg. per liter. Consolidated minerals were tested as 50-80 mesh particles, obtained by crushing and screening the rocks. Relative adsorptivities for the linear isotherms found in the low concentration region were, in increasing order: loess, sandstone, beachsand, arkose, limestone, silt, and greensand. Nonlinear isotherms were observed at higher concentrations with three of the sediments. Beachsand and sandstone were fit by Langmuir and Freundlich isotherms, respectively, but the loess isotherm had a relative adsorptivity which increased with concentration. Loess data were not fit by any of these isotherms.

THE SYSTEMS dodecylbenzenesulfonate-earth sediments were studied in connection with problems in pollution of groundwater by detergents. Specifically, equilibrium isotherms were measured and described.

Previous workers have described alkylbenzenesulfonate (ABS) adsorption on some solids as linear over wide ranges (*6*), as similar to that which follows the Freundlich isotherm (*10*), or as that determined by extrapolation (*7*). The data for ABS adsorption reported in this paper also serve to illustrate several well-known limitations to these special-case approaches.

Mass transfer rates are frequently proportional to the difference between the actual and equilibrium concentration—i.e., the concentration driving force. For this reason, equilibrium isotherms are useful in analyzing rate data using techniques developed for ion exchange and other fixed bed systems. For example, isotherms similar to those reported here would be useful in improving the interpretaton of the column elution data of Wayman, Page, and Robertson (*15*) and the adsorption rate data of Weber and Morris (*17*).

EXPERIMENTAL

Materials. The properties of the surfactant agent used, Nacconol NRSF, are available elsewhere (*2*); it contained 92.5% active sodium dodecylbenzenesulfonate (DDBS). The compound DDBS was used because ABS is the essential ingredient in "hard" detergents and because the largest volume production of ABS involves DDBS.

The seven earth sediments tested are shown in Table I. The unconsolidated sediments were chosen as representative of sediments found in the zone of aeration and the upper zone of saturation of groundwaters; the consolidated sediments were chosen as representative of the sedimentary rocks which are most prevalent on the earth's crust through which groundwater percolates. Shale was not included because of its relatively impervious nature.

Procedure. A predetermined amount of sediment (30, 60, or 100 grams weighed to 0.1 mg.) was mixed with an aqueous DDBS solution of predetermined volume (75 to 200 ml.) and concentration (5 to 100 mg. per liter) in a 500-ml. bottle and agitated for 3 hours with a stirrer (*11*).

Considerable time was then allowed to ensure that the mixture had reached equilibrium—a three-day shaking period, during which the mixture was shaken 5 minutes daily, and a four-day settling period which also provided time for defoaming. This seven days was sufficient to reach equilibrium for all substances except arkose; the time used for arkose tests was 12 days—five for shaking and seven for settling. The temperature was 75 ± 5° F.

The time required to reach equilibrium obviously depends on particle size, agitation, and other rate factors. The order of magnitude experienced in this work (3, 5, 5, 7, and 11 days for beachsand, greensand, sandstone, loess, and arkose, respectively) was approximately the same as the 6 + days for carbon (*17*), the several days to several weeks reported for clays by Suess (*10*), or the range of values reported by Wayman, Page, and Robertson, which were 2 days for Ottawa sand (*14*) and 12+ days for kaolinite (*16*). Time requirements as low as a few hours have been reported for carbon (*7*) and Ottawa sand (*4*).

The sulfonate (DDBS) concentration in the liquid phase at equilibrium was determined by direct analysis of a sample of the liquid. The sulfonate concentration on the solid phase at equilibrium was determined from a mass balance on the liquid phase—i.e., by the difference between the initial and final sulfonate content in the liquid. Thus, calculation of the solid concentration required measurement of the liquid volume and solid mass as well as an accurate measurement of the initial liquid concentration.

To estimate which initial conditions would result in the desired final concentrations, and to choose initial conditions to minimize the uncertainty in the calculated solid concentration, it was necessary to have some preliminary knowledge of the magnitude and shape of the adsorption isotherm. This is a common approach in batch adsorption isotherm measurements. This was done with two initial runs using 60 grams of solid and 100 ml. of solution containing 10 and 50 mg. per liter respectively.

Analysis. The methylene blue method (*1*, *3*, *8*, *5*, *13*) was chosen for analyzing the equilibrium liquid phase sample because the chloroform extraction step avoids the interference probelm involved in the direct utltraviolet method (See Appendix). For consistency, the liquid phase sample at initial conditions was analyzed by the same method. The standard methylene blue method of 1952 (*8*) was followed, but reproducible results were obtained (*11*) only after the cell sample rinsing step was omitted to prevent wall adsorption of the dye, the cotton was prewet with chloroform to minimize cotton adsorption of the dye, and the amount of cotton was reduced to about 150 mg. to minimize cotton adsorption of the dye while providing for removal of solid particles and water droplets (*9*).

A calibration was made at 650 mμ using cell lengths (*L*) of 1.0 and 5.0 cm. in a double beam spectrophotometer having

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absorance (A) scale divisions of 0.1 in optical density units. For the concentration (C) range of 5 to 50 mg. of DDBS per liter, the calibration was:

$$C = (46.3A/L) \pm 0.25 \text{ mg./liter} \qquad (1)$$

The uncertainity reported in Equation 1 is the average, absolute deviation (of known samples) from the calibration equation. Equation 1 indicates an extinction coefficient of 0.0216 liter per mg.-cm. Since solutions having 60 to 80 mg. per liter did not follow the linear Lambert-Beers model of Equation 1, solutions above 50 mg. per liter were diluted before analysis.

Reproducibility. Duplicate runs were made with several sediments to test reproducibility. Results, given in Table II, are expressed as variation in solid concentration, where the solid concentration is the ratio of mass of solute adsorbed to mass of solid. Also given for comparison are the estimated errors in solid concentration due to analysis; these were calculated by error propagation from the two liquid analyses using the uncertainty given in Equation 1.

The comparison in Table II indicates that the variation in duplicate runs was the same as (sandstone and limestone) or less than that estimated from analytical errors. Therefore, the controlling error or uncertainty was that of the liquid analysis.

RESULTS

Isotherms. Since the shape of the isotherm often depends upon the concentration range considered, the results are shown in plots of both low and high liquid concentrations.

The liquid-solid equilibria values in the low range are shown in Figure 1, which includes all seven sediments over the liquid concentration range of 1 to 16 mg. per liter. Equilibria values for liquid concentrations up to 45 and 87 mg. DDBS per liter are shown in Figures 2 and 3 respectively. Tabular values have been given in thesis form (*11*).

The median value of uncertainty in solid concentration, as calculated from liquid analyses, was ± 3% for the 49 runs made. The higher uncertainties all occurred at low liquid concentrations. Uncertainties were: 1 to 2% for silt and greensand except at the lowest concentration studied (where they were 6 to 7%); 1 to 3% for limestone, arkose, and loess except at the two lowest concentrations measured (where uncertainties were 7 to 10% for limestone and arkose and 13 to 20% for loess); and 3 to 6% for beachsand and sandstone except at the three lowest concentrations studied (where they were 8 to 13%).

As shown in Figure 1, all seven sediments followed linear isotherms in the low concentration region. The relative adsorptivity of each material, at a given equilibrium concentration of the liquid, is described by the b values shown in Figure 1, where b is defined by:

$$q = bC \qquad (2)$$

where q and C are equilibrium concentrations of the solid and liquid, respectively. The dash-line portions of the silt and greensand isotherms indicate that perhaps the isotherms are not linear in the very low concentration region; any conclusion concerning the region below 2 to 3 mg. per liter must be tentative, however, as only one datum point ws taken for each mineral in this low concentration range.

Figures 2 and 3 include all the equilibrium data obtained for each sediment reported; both figures are drawn with identical scales for comparison purposes. As shown in Figure 2, greensand, limestone, and arkose all have linear isotherms within the range studied. Slight differences in relative adsorptivities between Figures 1 and 2 reflect uncertainties in the data, but may also indicate some slight deviation from linearity.

Table I. Description of Earth Sediments Tested

Type	Name	Source(*12*)	Appearance
Unconsolidated	Silt	Monroe County, N. Y.	Mudlike
	Loess	Muscatine. Iowa	Mudlike
	Beachsand	Charlotte, N. Y.	Granular[a]
	Greensand (Glaconite)	Birmingham, N. J.	Partly Granular
Consolidated	Sandstone, Grey (Berea Girt)	Berea, Ohio	Granular[b]
	Limestone, Grey	Buffalo, N. Y.	Granular[b]
	Arkose	Mt. Tom, Mass.	Granular[b]

[a] Mainly 40–80 mesh.

[b] 50–80 mesh obtained by screening particles which resulted from crushing and grinding the rock.

Table II. Reproducibility Indicated by Repeatability Tests

		Conditions			Liquid Conc.		Solid Conc. at Equil.		
Sediment	Run No.	Solid, grams	Liquid, ml.	Time, hrs.	Initial, mg./l.	Equil.(c), mg./l.	Conc.(q), mg./kg.	Est. error by anal.	Variation in duplicate tests
Greensand	GS5	59.985	135	210	60.4	4.6	125.6	±0.9%	±0.2%
	GS6	59.978	135	220	60.4	4.8	125.1	±0.9%	
Beachsand	BS3	59.990	85	190	8.2	2.9	7.37	±9.6%	±4.9%
	BS4	59.985	85	188	8.1	3.15	7.02	±10.1%	
Sandstone	SA2	29.914	100	236	49.2	37.2	40.1	±4.2%	±5.1%
	SA3	29.914	100	237	49.2	37.8	38.1	±4.4%	
Arkose	AR2	30.028	100	288	49.2	28.8	67.9	±2.4%	±0.0%
	AR3	30.031	100	289	49.2	28.8	67.9	±2.4%	
Limestone	LM2	30.026	100	238	49.2	22.8	87.9	±1.9%	±2.3%
	LM3	30.028	100	239	49.2	23.4	85.9	±1.9%	

Two of the nonlinear isotherms in Figure 3—beachsand and sandstone—have slopes which decrease with increasing concentration; on the other hand, loess exhibits an isotherm with an increasing slope.

Analytical Expressions. The seven isotherms were fit to empirical equations to describe functional dependance of $q = q(c)$ quantitatively and for interpolation purposes. All isotherms were fit using the criterion of minimum sum of the deviations. The constants for the one-constant linear isotherm defined by Equation 2 are given in Figure 2 for three sediments and in Figure 1 for silt.

The beachsand appeared to have the shape of a Langmuir isotherm, which is a one-constant model where the upper limit of either solid or liquid concentration is specified; where upper limits are not specified, the Langmuir isotherm may be expressed by the following two-constant form: .

$$q = \frac{mC}{1 + nC} \tag{3}$$

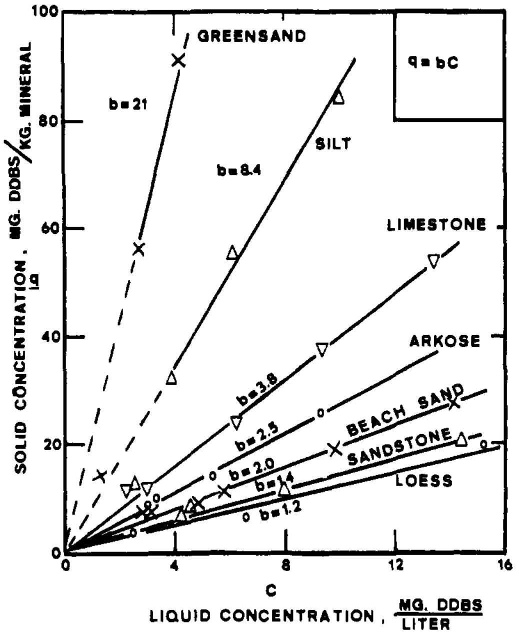

Figure 1. Low concentration isotherms

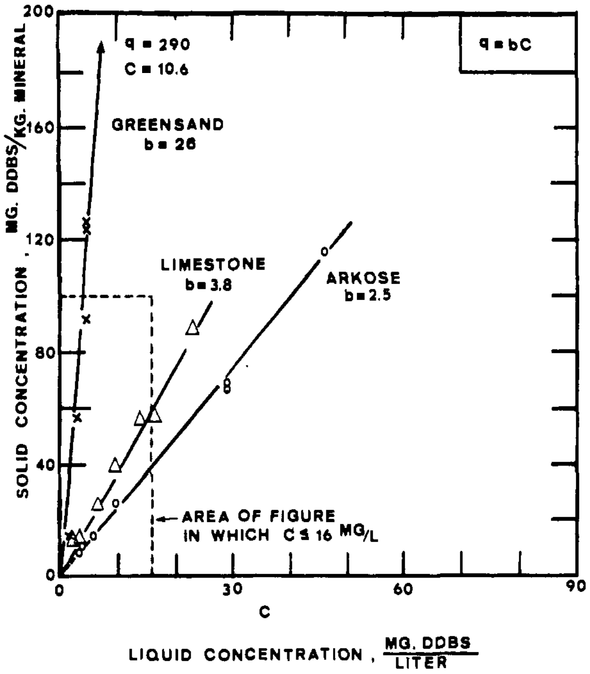

Figure 2. Linear isotherms

The beachsand isotherm was fit successfully by Equation 3, as shown in Table III. Also shown in Table III are the linear isotherms, for which $n = 0$.

The sandstone was fit satisfactorily by the Langmuir isotherm, as shown in Table III; however, the following Freundlich isotherm gave a slightly better fit:

$$q = 2.4C^{0.77} \tag{4}$$

The problem of finding a form for fitting the increasing slope data of Loess was resolved by using negative value for n in the Langmuir isotherm, Equation 3. See Table III.

DISCUSSION

The shapes and limitations of isotherms are well known to many. Isotherms are usually first order (Langmiur) or second order (Sigmoidal) and care must be exercised to avoid the pitfalls of extrapolating the special-case approximations (linear and power-law or Freundlich). Since several aspects of isotherms have apparently been passed over in the literature on ABS adsorption, however, it is useful to discuss some specific examples.

Comparisons. A review of several solids by Wayman (*14*) lists equilibrium adsorbed amounts (q values) at initial, nonequilibrium liquid concentrations. The usefulness of this list would be improved if equilibrium values of both phases were given; even more useful would be Table III-type interpolation formulae or at least a comparison at constant equilibrium liquid composition. Where suitable interpolated limits are specified, the linear result form of Klein, Jenkins, and McGaukey (*6*) and Equation 2 is the best comparative form, provided it has been found applicable in experiments such as those reported in Figure 1.

In some cases, the list noted above includes only one equilibrium point for a given system. The variation in isotherm shapes, shown here by loess, greensand, and beachsand, illustrate that little information regarding equilibrium relationshps may be assumed from such evidence.

Capacity. The phrase "ultimate capacity" has unfortunately been used by Joyce and Sukenik (*7*) and others to describe one point on an isotherm—the q value at a specified liquid concentration. Furthermore, this point has often been estimated (*7*) by extrapolation on the empirical basis of a log–log plot without

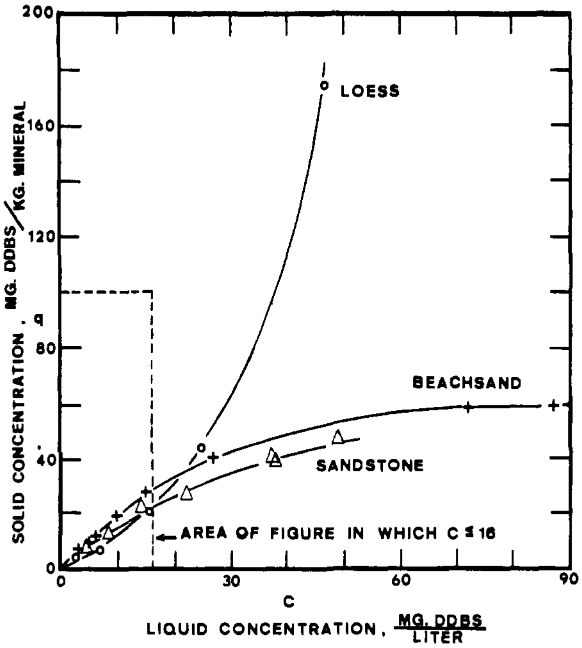

Figure 3. Nonlinear isotherms

Table III. Constants for Langmuir-Type Isotherms

	Constants, Eq. 3		Total Range Covered		Range of Better Agreement	
Mineral	*m*	*n*	Mg./liter[a]	Av. rel. dev.[c]	Mg./liter	Av. rel. dev.[c]
Arkose	2.5	0.0	3–46	±8%	5–46	±6%
Limestone	3.8	0.0	3–23	±5%	...	...
Silt	8.4	0.0	4–10	±3%	...	...
Greensand	26.	0.0	3–11	±11%	5–11	±3%
Beachsand	2.8	0.0342	3–87	±9%	10–87	±4%
Sandstone[b]	1.7	0.0155	4–48	±5%	...	...
Loess	1.0	−0.0101	3–4	±13%	15–46	±6%

[a] Values at $c = 1.5$ to 2.5 mg./liter were not included as deviations were large; thus, the lowest value was omitted for limestone, silt, greensand, and loess.

[b] Using Freundlich isotherm, Equation 4, the average relative deviation was ±4%.

[c] This deviation is that between the analytical expression and the data.

experimental justification. With the concentration of one or two samples, the same number of runs could be used to define a complete isotherm over the entire region of interest similar to that reported in this paper. All the benefits of a general isotherm would accrue, including provision for interpolation instead of an extrapolation of unknown validity.

Lack of Generality. Whereas the Freundlich function is known to be unreal at both zero and high concentrations, it is the form in which ABS results are presented in several articles (*7*, *10*). For some systems, the latter assumption of no upper limit on q is not so important practically. Such limits have been observed with ABS–solid systems however—e.g., with beachsand (Figure 3) and Ottawa sand (*4*). The occurance of such limits would invalidate extrapolations such as noted in the preceding paragraph.

A well known and important practical limitation of the Freundlich form is its lack of reality at decreasingly small concentrations. Frequently, the linear isotherm is applicable instead (See Sandstone Figure 1 and 3). However, there are also pitfalls with linear models. Klein, Jenkins, and McGauhey (*6*) studied five California soils and concluded that "absorption isotherms for ABS are linear up to 100 mg. per liter." The curved isotherms at 30 mg. per liter in Figure 3 indicate that their conclusion is not generally applicable.

Flow Studies. In transient rate tests (elution of fixed beds) Wayman, Page, and Robertson (*15*) found greensand was more effective than beachsand or loess for sulfonate removal. Such rate studies need equilibrium data for proper evaluation: for example, results reported as b values in Figure 1 probably indicate a primary reason for the ranking in effectiveness, even though the sediments are not directly comparable.

Prediction of the significance of each sediment in removal of ABS in the zone of aeration requires rate data for flowing liquids and mineral content information in addition to this equlibrium study; thus, no definite conclusion may be drawn. However, some indication of the sediments which have the highest removal potential is shown by the rank of b at the low concentrations found in nature (Figure 1).

APPENDIX—ULTRAVIOLET ANALYSIS

A calibration for DDBS in distilled water was made at the absorption peak in the ultraviolet region (224 mμ) using a 1.0-cm. cell. For the 5 to 30 mg. of DDBS per liter range, it was:

$$C = (26.9A/L) \pm 0.13 \text{ mg. per liter} \qquad (5)$$

The notation is the same described in the text near Equation 1. Equation 5 indicates an extinction coefficient of 0.0372 liter per mg.—cm. A deviation of about 3% was noted at 50 mg. per liter.

This UV measurement method is more sensitive and more precise for binary mixtures of DDBS and water than the methylene blue method. It was not used for earth sediment tests, however, because of interference from fine particles and dissolved material in the equilibrium sample.

ACKNOWLEDGMENT

This work was supported by the Connecticut State Water Resources Commission.

LITERATURE CITED

(1) Abbott, D. C., *Analyst* **87**, 286 (1962).
(2) Allied Chemical Corporation, National Aniline Division, New York, N.Y., *Bull C-4*, 1960.
(3) Degens, P. N., Zee, H. V., Kommer, J. D., *Sewage Ind. Wastes* **25**, 20 (1953).
(4) Ewing, B. B., Lefke, L. W., Banerji, S. K., *Robert A. Taft. Sanitary Eng. Center Symp., Tech. Rep.* **W61-5**, 166 (1961).
(5) Fairing, J. D., Short, F. R., *Anal. Chem* **28**, 1827 (1956).
(6) Klein, S. A., Jenkins, D., McGauhey, P. H., *J. Water Pollution Control Federation* **35**, 636 (1963).
(7) Joyce, R. S., Sukenik, V. A., *U. S. Public Health Service Publication* **999-WP-12**, AWTR-10, May 1964.
(8) *Sewage Ind. Wastes* **24**, 658 (1951).
(9) Short, F. R., Monsanto Research Laboratory, Dayton, Ohio, personal communication, June 1963.
(10) Suess, M. J., *J. Water Pollution Control Federation* **36**, 1393 (1964).
(11) Tan, J. K., M. Engr. thesis, Yale University, January 1964.
(12) Ward's Natural Science Establishment, Rochester, N. Y., pp. 63–68 Geology Cat. **628** (1962).
(13) Wayman, C. H., *U. S. Geol. Survey Profess. Papers* **450**, Art. 49, B117 (1962).
(14) *Ibid.*, Art. 117, C137 (1962).
(15) Wayman, C. H., Page, H. G., Robertson, J. B., *U. S. Department the Interior, FHA Tech. Rep.* **532**, February 1965.
(16) Wayman, C. H., Robertson, J. B., Page, H. G., *Ibid.* Art. 238, E 181 (1962).
(17) Weber, W. J., Morris, J. C., *J. Sanit. Eng. Div. Am. Soc. Civil Engrs.* **90**, SA3, 79 (1964).

RECEIVED for review January 11, 1965. Accepted December 21, 1965.