The Correlation of Washability with the Rate of Surfactant Adsorption

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Abstract

A relation between the rate of adsorption of surfactant molecules at a gas-liquid interface and the soil removal ability of the surfactant solution is presented. The relation is of the form

$$SR = A + Bk + Ck^2$$

where SR is the percentage soil removed, A, B, and C are constants, and k is the first order rate constant for the adsorption process. The relation is empirical and as yet has not been coupled with a fundamental explanation of the detergency process on a molecular scale.

The maximum soil removal does not always occur at the highest rate constant but may reach a maximum at an intermediate value. The soil removal process seems to be different above the CMC than below it. For the different surfactants studied, the soil removal is higher for the surfactant with larger rate constants.

The rate of surfactant adsorption was obtained from dynamic surface tension measurements made with the oscillating jet technique. Soil removal information was obtained from laboratory tests using a Terg-O-Tometer and reflectance measurements on standard cloth swatches. Cationic, nonionic, and anionic surfactants were studied. Specifically, the surfactants were Triton X-100 (an octyl phenol with 8 or 9 ethylene oxide units), NaDBS (sodium dodecylbenzene sulfonate), and CTAB (cetyl trimethylammonium bromide). The surface tension time range of 5 to 60 milliseconds and soil removal ability of these surfactants was investigated over the temperature range of 20 to 60C, and the concentration range of 0.0003 to 0.009 M.

Introduction

FOR MANY YEARS investigators have attempted, with little or no success, to relate the physical and chemical properties of detergent systems to their soil removability. Various properties such as surface tension, micelle size, ionic charge, etc., have been studied. General rules for detergent formulation have been developed, and most presently used detergents have been formulated on the basis of these general rules.

However, it would be advantageous to be able to measure some property of a detergent solution and then predict its soil removability. This property might ultimately be related to the molecular structure of the detergent constituents. The next step would then be to construct a detergent that possessed those properties which would maximize soil removal. In this paper we present work which we feel is a step, perhaps only a small step, toward the ultimate goal of building a detergent to certain specifications.

The physical property investigated during this study was the rate of surfactant adsorption at the gas-liquid interface. The rate of surfactant adsorption is closely related to the surface tension of the solution as a function of time. It has been well known for some time that an aqueous solution of a good detergent must have a low surface tension. However, it has not been possbile to relate surface tension directly with soil removal. It seemed possible that rate of surface tension lowering might be the important parameter in soil removal. The experimental method used to obtain the desired information was the oscillating jet technique for obtaining dynamic surface tension. The systems studied contained only surfactant and no other additives.

Experimental

Dynamic Surface Tension

The oscillating jet technique for measuring surface tension was put on a fairly sound theoretical basis by Bohr (1) in 1909. Since that time, it has been used by numerous investigators with most of the recent interest being on dynamic rather than static surface tension. The method consists of forcing a liquid through an elliptical opening by applying a constant pressure. The resulting liquid stream exhibits a stationary wave pattern along its longitudinal axis. The cross section of the stream oscillates from an ellipse with its major axis parallel to that of the elliptical opening to an ellipse with its major axis perpendicular to the major axis of the opening.

Bohr related the wavelength of these stationary waves to the surface tension of the issuing liquid. The other experimental parameters needed in Bohr's relation are viscosity, density (liquid and gas), maximum and minimum stream diameter, and flow rate. The experimental methods used for obtaining all of these parameters are similar to those described by Netzel (2). In fact, much of the apparatus used was the same as Netzel used. Three major alterations were made in the system: 1) The elliptical orifice was changed from a flat plate to a tube and made larger. 2) The stream was vertical instead of horizontal. 3) The constant head liquid supply was similar to one used by Defay and Hommelen (3) and was water-jacketed for constant temperature purposes.

Range of Variables

The flow rates studied varied between 3.4 g/sec and 3.6 g/sec. The reproducibility of these measurements was generally ±0.1%. The orifice used had a maximum diameter of 0.175 cm and a minimum diameter of 0.144 cm. The experiments were run at approximately 20, 30, 40, 50, and 60C, and the temperature was constant to within ±1C. The concentrations studied were 0.0003, 0.0009, 0.0015, 0.0030, and 0.0090 moles/liter. The solutions were all made using distilled water. The time range covered was 5–60 milliseconds.

Surfactants

The surfactants were used as obtained from the manufacturer. The Triton X-100 and the NaDBS (which was Siponate DS-10) were of at least 98%

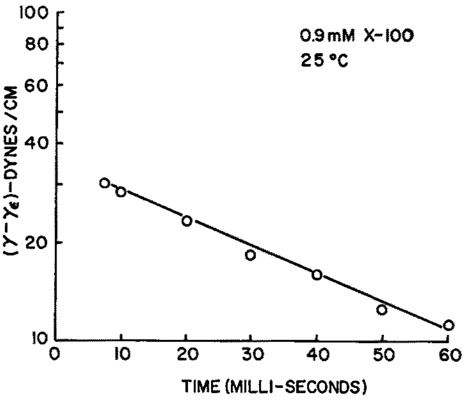

FIG. 1. The difference between dynamic and static surface tension as a function of time for a 0.9 mM solution of Triton X-100 at 25C.

purity. The CTAB was Bromat which contained an active bromide content of 98%.

Washing Tests

The washing tests were run in a Terg-O-Tometer at 20, 40, and 60C. The surfactant concentrations used were 0.0003, 0.0009, 0.0015, 0.0030, and 0.0090 moles/liter. Deionized water was used with the anionic and nonionic surfactants, and distilled water was used with the cationic surfactant. Ten 4 in. × 4 in. swatches were washed per liter of washing solution.

The soil cloth used was a clay cloth that has been specially developed by Whirlpool Corporation to give good simulation of practical soiling. An agitation rate of 100 strokes per minute was used for 10-min wash cycles. All rinses were 5 min long with no agitation at 20C. Drying was done in a home drier, and all runs were made in triplicate. A complete presentation of the washing data is given in Table IV.

Discussion

Rate Constants

The rate for adsorption of surfactant molecules into a liquid-gas interface may be obtained by measuring the surface tension of the solution of interest as a function of time. For many surfactants of commercial interest this rate is so rapid that a method of measuring surface tensions in the millisecond range must be used. The oscillating-jet technique is such a method.

This method has a number of drawbacks such as the fact that Bohr's mathematical model does not adequately fit the experimental situation. However, with suitable empirical or semitheoretical corrections the method does yield dynamic surface tension data which will give information about rate of surfactant adsorption. The method of correction which we have chosen is that of Thomas and Potter (4). The correction factors obtained for the particular orifice used in these experiments are given in Table I. To obtain the true value of the surface tension it is necessary to multiply the value calculated from Bohr's relation by the correction factor.

TABLE I
Oscillating Jet Correction Factors

Time, sec	Correction Factor
0.005	0.77
0.010	0.83
0.020	0.90
0.030	0.94
0.040	0.97
0.050	0.99
0.060	1.00

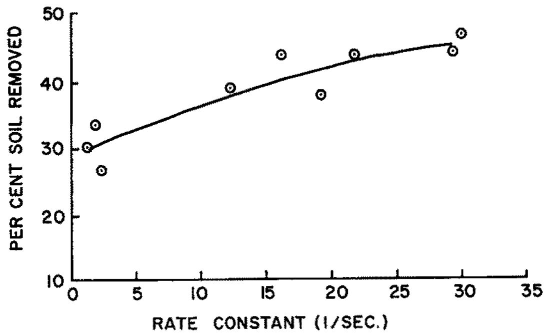

FIG. 2. Soil removal as a function of the rate of surfactant adsorption for Triton X-100 above the CMC.

The rate of adsorption was calculated from the corrected dynamic surface tension (DST) values by assuming that the process was of the first order. Various other orders were studied but none fit the data as well as the first order. The equations used to calculate the rate constants are:

$$\frac{d(\gamma - \gamma_e)}{dt} = k(\gamma - \gamma_e)$$

$$\therefore \; Ln(\gamma - \gamma_e) = -kt + C$$

Where γ = corrected dynamic surface tension
γ_e = equilibrium surface tension
k = first order rate constant
t = time
C = constant of integration

If the log of $\gamma - \gamma_e$ is plotted versus time the slope of the resulting curve is the rate constant. Fig. 1 is an example of the type curve the rate constants were obtained from.

The intercept C should be $\gamma_o - \gamma_e$ where γ_o is the surface tension of pure water. However, the experimental C was almost always smaller than $\gamma_o - \gamma_e$, and it appears that the adsorption process might be two different and consecutive first order processes. The rate constants calculated by Netzel (2) for Triton X-100 over the time range 1–5 milliseconds were much higher than the rate constants obtained in this study. His findings would also support the idea of two different first order processes. The rate constants obtained in this study are presented in Table II.

Correlation

The correlation that has been obtained is empirical and was obtained by plotting the rate constant obtained under given conditions of temperature, con-

TABLE II
First Order Rate Constants for Surfactant Adsorption at a Gas-Liquid Interface

Concentration, mM	Temperature, C	Rate constant (sec $^{-1}$)		
		X-100	NaDBS	CTAB
0.3	20	2.4		4.3
	40	1.9		1.8
	60	1.3		0.25
0.9	20	19.2	4.4	12.8
	40	21.8	1.8	7.8
	60	29.3	0.5	3.9
1.5	20	12.2	9.4	18.0
	40	16.2	6.9	14.8
	60	30.0	4.4	11.8
3.0	20		14.0	13.1
	40		6.1	7.1
	60		2.6	2.4
9.0	20		11.0	
	40		6.1	
	60		2.6	

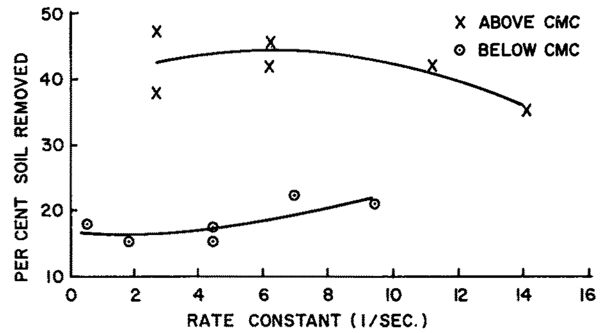

FIG. 3. Soil removal as a function of the rate of surfactant adsorption for NaDBS.

centration, and surfactant versus the amount of soil removed under the same conditions. These plots are presented in Fig. 2 to Fig. 4. The lines drawn through the points are quadratic least squares curves of the form

$$SR = A + Bk + Ck^2$$

Where SR = per cent soil removed
A,B,C = constants
k = rate constant

The values for A, B, and C plus the standard deviation and a coefficient of correlation for each line are given in Table III.

There seems to be a change in the soil removal and adsorption process near the critical micelle concentration (CMC) because different curves were obtained above and below the CMC. There is only one curve for X-100 because all of the data were taken above the CMC of this surfactant. There is also some question about CMC's as applied to nonionic surfactants. The fact that there is a change in soil removal above and below the CMC is not surprising. It is well known that many properties such as surface tension change rather suddenly when the CMC is reached.

TABLE III
Statistical Parameters for Soil Removal Correlation

Surfactant	Constants A	B	C	Standard deviation	Coefficient of correlation
X-100	28.64	0.96	−0.013	3.19	0.921
NaDBS					
Above CMC	39.25	1.65	−0.136	4.14	0.706
Below CMC	16.81	−0.23	0.068	2.45	0.753
CTAB					
Above CMC	14.78	2.13	−0.105	2.89	0.780
Below CMC	4.20	2.33	−0.088	3.01	0.920

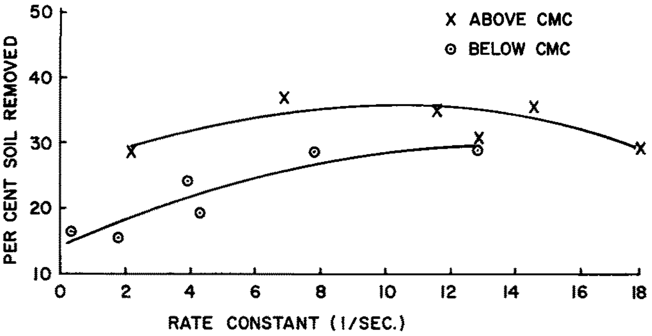

FIG. 4. Soil removal as a function of the rate of surfactant adsorption for CTAB.

Even though the correlation is empirical, a few comments can be made about its fundamental significance. The transport properties of the surfactant molecule must be important because the rate of adsorption depends in part on the diffusion coefficient. We know that the diffusion coefficient depends on the size, shape, and intermolecular potential of the solute. The solvent properties are also important but since water is the solvent in all cases, the solvent would be important only in the differing effects it has on each solute. Thus the fundamental molecular parameters that affect diffusion must also affect detergency.

The soil removal is higher above the CMC, but rate constants can be lower than they were below the CMC. This indicates that the process of adsorption is different above and below the CMC. The reduction in rate constant might be due to the increased size of the diffusing specie (the micelle) or it might be due to an increased electrostatic barrier at the surface.

ACKNOWLEDGMENT

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TABLE IV
Washability Data[a]

Surfactant conc	20C						40C						60C					
	NaDBS		X-100		CTAB		NaDBS		X-100		CTAB		NaDBS		X-100		CTAB	
	% S.R.	S.D.	% S.R.	S.D.	% S.R.	S.D.	% S.R.	S.D.	% S.R.	S.D.	% S.R.	S.D.	% S.R.	S.D.	% S.R.	S.D.	% S.R.	S.D.
0.3 mM	15.4	2.67	26.7	3.16	9.5	1.80	17.8	1.83	33.6	3.17	5.82	2.00	19.7	1.95	30.2	2.07	6.6	1.85
0.9 mM	15.5	1.49	38.0	2.89	19.2	2.73	15.4	2.65	44.0	1.90	18.0	3.14	18.0	2.48	44.5	1.60	14.4	3.01
1.5 mM	21.1	1.82	39.2	1.67	19.5	2.45	22.4	2.07	44.1	2.13	25.7	2.87	17.6	2.19	47.1	1.93	25.3	3.74
3.0 mM	35.3	2.58	40.1	2.48	21.0	2.57	41.9	2.22	46.2	2.46	26.9	2.50	38.2	1.81	48.2	2.02	18.5	2.42
9.0 mM	41.9	2.39	42.6	2.09	25.7	3.77	45.8	2.64	46.6	2.44	26.7	1.97	47.4	2.02	50.0	1.99	18.5	2.16

[a] The % of S.R. refers to per cent soil removed; S.D. refers to standard deviation.

NOTE: 1) 0.3 mM corresponds to 0.019% X-100, 0.010% NaDBS and 0.011% CTAB. 9mM corresponds to 0.58% X-100, 0.31% NaDBS and 0.33 % CTAB.

2) The CMC for X-100 is about 0.25 mM at 25C (see Ref. 5); varies from 3 mM at 25C to 5 mM at 75C for NaDBS (see Ref. 6) is about 0.9 mM at 25C for CTAB (see Ref. 6).