Adsorptivity and Rinsability of Built Detergents Using Radiotracers. I

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Abstract

Linear, primary alcohol sulfates and linear alkylbenzene sulfonates tagged with radioactive sulfur or, in one case, tritium, were employed to determine adsorptivity and rinsability characteristics.

In the rinsability studies it was found that when using scoured cotton as substrate the linear, primary alcohol sulfates leave a slightly lower residue than the sulfonates. Both surfactants almost reach an equilibrium after the first wash-dry cycle. The surfactants are present on the surface in a reversibly adsorbed state as shown by exchange experiments with unlabelled surfactants.

In the adsorption experiments, run under the same conditions as the rinsability experiments, Langmuir-type isotherms are obtained whose equilibrium values are comparable to the rinsability values.

The effect of free detergent alcohol concentration on adsorptivity and rinsability in linear, primary alcohol sulfate built detergent formulations was also studied.

Introduction

THE CURRENT INTEREST in the use of soft, or easily biodegradable detergents has initiated considerable research and development. Other properties besides easier biodegradability are of interest in a detergent, such as detergency, foamability, and rinsability. The latter is defined as the amount of surfactant remaining on a selected fabric after a complete washing cycle in an automatic washer. Rinsability is, of course, related to adsorptivity, hence some knowledge of the adsorption characteristics of a surfactant intended for commercial development is desirable in that one can obtain some insight into its performance relative to other well-established materials.

To facilitate such studies a radiotracer approach is most attractive because it minimizes analytical method development time, it is free of interferences, it is capable of very high sensitivity and, with modern automatic counting and computing methods (1), it yields large numbers of analyses at very low cost. The use of radio-labelled surfactants to study adsorption is well documented (2–5).

In the present study four labelled surfactants were prepared, two sodium alkyl sulfates and one sodium linear alkylbenzene sulfonate labelled with sulfur^{35} and one sodium linear alkylbenzene sulfonate labelled with tritium. One of the alkyl sulfates was prepared from a linear, primary alcohol fraction intended for commercial development and one from a laboratory fraction. The first alcohol covered the carbon number range C_{12} through C_{15} (Neodol 25-S, Shell trademark), the second C_{14} to C_{15} (Neodol 45-S). These will be referred to as C_{12}–C_{15} sulfates and C_{14}–C_{15} sulfates. The linear alkylbenzene sulfonates (C_{13} side chain) will be referred to as LAS and where the tritium-labelled one is used, it will be so designated. The tritium-labeled sulfonate was prepared to permit a rinsability competition experiment between the sulfonate and C_{14}–C_{15} sulfate. The modern liquid scintillation counter can readily analyze for both tritium and sulfur^{35} on the same cotton sample.

Radiochemical Purity

Surface chemistry studies are particularly sensitive to impurities since only a small fraction of the bulk surfactant is involved in the adsorption. Radioactive compounds may contain contaminants in trace amounts but of sufficient radioactivity to invalidate the results (6). Hence, it was necessary to establish that the radiochemical purity of each surfactant would be sufficient for the experiments described below. This was done by the use of paper chromatography described elsewhere (1), and exchange experiments described below. Furthermore, the probability of interference by such contamination was reduced by synthesizing the labelled compounds in a reasonably low specific activity so that only nominal dilution with *inactive* surfactant was required for the rinsability studies and no dilution at all was required for the adsorption studies.

Analytical Method

While the details of the analytical method will be reported elsewhere (1), a brief description is in order. In the rinsability studies 0.5 g samples were cut from a number of the washed and dried diapers and towels. These were immersed in 20 ml of dioxane-based liquid scintillator (80 g naphthalene, 4 g 2,5-diphenyloxazole,[1] 0.1 g dimethyl POPOP [1]/liter of 10% water in dioxane). The surfactant concentration, in parts per million, was obtained from the radioactivity of these samples measured by counting the immersed samples in the liquid scintillation counter. In the adsorption studies aliquots of the solution were dissolved in the dioxane scintillator and counted. Adsorbed surfactant was obtained from the decrease in solution concentration.

Rinsability Studies

Experimental

Materials—Anionic Surfactants

a) Sodium C_{14}–C_{15} sulfate-S^{35} labelled.
b) Sodium C_{12}–C_{15} sulfate-S^{35} labelled.
c) Sodium linear alkylbenzene sulfonate-S^{35} labelled.
d) Sodium linear alkylbenzene sulfonate-tritium labelled.
e) Composition of the wash solution was as follows: surfactant, 0.4 g/liter; sodium tripolyphosphate, 0.9 g/liter; sodium silicate, 0.31 g/liter; sodium sulfate, 0.46 g/liter, in water of 150 ppm hardness.

[1] Available from Packard Instument Co., Downers Grove, Ill.

f) Sebum—synthetic soiling mixture (11). Use 50 g/8 lb of cloth. Added manually to fabric by smearing with a spatula.

Equipment

a) Washer: Sears, Roebuck 1964 Lady Kenmore Model 800 top-loader, agitator type.
b) Dryer: Sears, Roebuck 1964 Lady Kenmore Model 800; electrically heated.
c) Diapers: bleached, cotton—Curity.
d) Towels: bleached, cotton, terrycloth hand towels—Dundee and Royal Terry.
e) Packard Liquid Scintillation Counter Model 3214 coupled to an IBM-026 card punch, Packard Instrument Co., Downers Grove, Ill.

Rinsability Method

The washer controls were set ("A" setting and "Hi" water level), and 140F water of known hardness was added to an 18.0 gal mark. The builders plus surfactant were added and the solution agitated for 1 min before adding an 8 lb load comprised of 25 diapers and 21 towels (all previously washed in the Kenmore 5 times with sodium tripolyphosphate, 100 g in 18 gal of water). After the washer had made its complete cycle (20 min washing period) the diapers and towels were dried (70 min; "Maximum Auto Dry" set at "On") in the dryer.

Wash solution samples were collected just before the towels and diapers were added and when the wash cycle had ended. The rinse water (the spray rinses plus the deep rinse) was discharged into a 55 gal drum containing a polyethylene bag liner, mixed and sampled.

One 0.5 g randomly-located sample of fabric was cut from each of ten identified diapers and ten identified towels after removal from the dryer and analyzed as described above. The remaining 15 diapers and 11 towels served merely as ballast.

Rinsability Results

In any tracer study involving as complex an operation as goes on in a household washer, a material balance based on radioactivity around the system is desirable to provide confidence in the data. These, in fact, were run for most of the rinsability experiments and some of the data are reported in Table I. Considering the inaccuracies in estimating the volume involved, the agreement in material balance is satisfactory.

The increase in surfactant concentration on the fabric due to the retained rinse water, which is evaporated in the dryer, is very small, assuming a retained weight of water equal to the fabric one calculates (from the concentration of surfactant in the total rinse water) that less than 0.1 g surfactant is so deposited on the fabric.

TABLE I

Material Balance: Radioactive Surfactant in the Washing System

Item No.	Active Matter	C_{14}–C_{15} Sulfate	Sulfonate	
	Group number, Table II	2	4	5
	Material analyzed	Grams of detergent, averaged over 4 washes/group		
1	Wash water before fabrics added	26.5	28.0	27.9
2	Wash water at end of wash cycle	24.9	27.1	26.7
3	Rinse water	2.3	1.6	2.5
4	Fabric	3.7	4.7	4.2
5	Total = Items 2 + 3 + 4 less surfactants carried over on cloth from previous wash [a]	28.2	29.7	29.3
6	Grams surfactant actually added	27.4	27.4	27.4

[a] Except for the first wash, every wash carried with it some surfactant. This quantity was calculated from the concentration and the weight (8 lb) of fabric. It was then subtracted from the total as shown above.

Rinsability experiments were run under different conditions of cleanliness with all but one of the labelled surfactants (tritium labelled). Generally, four complete cycles were run on a single loading of fabric in order to see if a steady buildup of residue occurs or if an equilibrium is reached. The data, in Table II, answer a number of questions. First, the two alkyl sulfates and the linear alkylbenzene sulfonate leave comparable residues on cotton with the sulfonate showing slightly higher values. Second, residue values after the first wash are almost at equilibrium, a small increase occurring during subsequent washes. Third, the presence of soil (sebum) has no significant effect on the amount of residue. The raw data also revealed a large variation between diapers or between towels. That is, those fabrics which initially had high or low surfactant residues tended to be those which had high or low residues through each of the four washes. Analysis of the data for one group of diapers carried through four washes gave a high correlation coefficient (0.7–0.8) which supports the preceding statement. This finding is further supported in the next section.

Rinsability Precision and Accuracy

The analytical method developed for this analysis is precise to ca. 1% and accurate to 2% (1). Therefore, variations in the sets of analysis from each wash number were due predominantly to variation in the residue concentration between and within diapers and between and within towels. The relative standard deviation of the average concentration of residual surfactant was 9%. The 95% confidence level was thus ±18%, and the least significant difference was 25.4%.

Table III shows the significantly higher variation *between* diapers and towels over that *within* them, indicating again the significant difference in surface characteristics from item to item. The accuracy of the method, that is, whether the use of average values of residue is reasonable, is supported by the data in Table I showing good material balance based, in part, on the quantity of adsorbed surfactant per batch.

Competitive Rinsability

To determine whether in a mixture of sodium alkyl sulfate and sodium linear alkylbenzene sulfonate one would monopolize the surface of the cotton, a two-

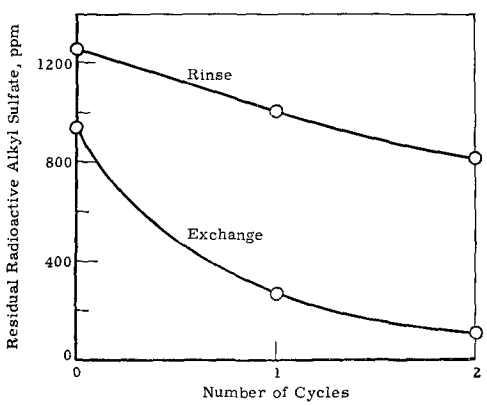

FIG. 1. Rinse and exchange with diapers containing radioactive C_{14}–C_{15} sulfate.

TABLE II

Effect of Repeated Laundering on the Amount of Residual Surfactant

Group No.	Active matter	Radio-active element	Water hardness,[a] ppm	Soil [b]	Sub-strate [c]	Residual Surfactant, ppm				
						1 [d]	2	3	4	Avg [e]
1	C_{14}–C_{15} sulfate	S^{35}	140–150	None	D	1120	1252	.....	.....	1186
					T	1041	1126	.....	.....	1084
2	C_{14}–C_{15} sulfate	S^{35}	140–150	Sebum	D	948	1101	979	1064	1023
					T	930	1034	941	1036	985
3	C_{12}–C_{15} sulfate	S^{35}	140–150	None	D	929	1002	.....	.....	965
					T	859	912	.....	.....	885
4	LAS	S^{35}	140–150	None	D	1139	1284	1337	1302	1266
					T	959	1031	1130	1081	1050
5	LAS	S^{35}	140–150	Sebum	D	1124	1408	1375	1500	1352
					T	830	1029	1027	1046	983

[a] Expressed as $CaCO_3$, Ca/Mg = 60/40.
[b] Sebum: clothes soiled with 50 g (60 ml) of synthetic sebum.
[c] Cotton: D = diaper; T = towel.
[d] Wash number.
[e] Estimated relative standard deviation (s) = 9% of average. 95% Confidence limits = ±18% of average. Least significant difference at the 95% confidence level = 25.4% of average.

wash test was conducted using a 50/50 w/w mixture of C_{14}–C_{15} sulfate-S^{35} labelled and LAS-H^3 labelled (total surfactant concentration = 0.4 g/liter). Analysis of both isotopes was performed by liquid scintillation spectrometry (8) and the data are shown in Table IV.

Table IV shows that the rinsability of a 50/50 mixture of C_{14}–C_{15} sulfate and LAS is not significantly different from that which could be expected from the rinsability of the unmixed surfactants.

To demonstrate that the surfactant is not irreversibly fixed to the cotton surface, two experiments were run; one where a batch of diapers and towels, after four washings with labelled C_{14}–C_{15} sulfate, was washed two additional times using unlabelled surfactant, and the second where a batch of diapers and towels, again, after four washings with labelled C_{14}–C_{15} sulfate went through two additional rinsing cycles (about 2 min per cycle) in the washing machine. The data for diapers are in Figure 1. The reversible nature of the adsorption is clearly evident in the exchange curve. The fact that the residue concentration does not fall after each exchange to about one-seventh of its previous value (the ratio of adsorbed to dissolved surfactant) shows that true exchange equilibrium has not been reached with each washing cycle. Rinsing is far less effective than exchange as expected from highly surface active materials. Findings with towels were similar to those with diapers.

Effect of Free Alcohol

Since the sulfates are made by sulfation of alcohols, it is likely that some unreacted alcohol may be present in the commercial product. Furthermore, small quantities of free alcohol are known to promote foaming. Therefore, some rinsability studies were made with the C_{12}–C_{15} sulfates containing varying amounts of free alcohol. All runs were at 150 ppm hardness with scoured diapers and towels. The same formulation was used as in the runs shown in Table II. Several comparison experiments demonstrated that the rinsability and adsorption properties of both alkyl sulfates (C_{12}–C_{15} and C_{14}–C_{15}) were the same.

It seems clear from Table V that a substantial (i.e., ca. 13%) amount of free alcohol increases the retention of surfactant. Examination of the raw data (the data in Table IV are again all averages of ten samples each) revealed that the precision of the runs with 8 and 13% alcohol was much poorer than with 1.1 and 3.3% alcohol. These two effects are believed to be due to the formation of an insoluble alcohol/alkyl sulfate adduct as described by Epstein and co-workers (9). They isolated a crystalline precipitate from the system lauryl alcohol/sodium lauryl sulfate of 1:2 mol ratio. This precipitate formed more easily at higher alcohol concentrations. The presence of such a precipitate would be expected to cause higher and more erratic retention over simple adsorption.

TABLE III

Analysis of Variance (7) Summary of the Residual C_{14}–C_{15} Sulfate on Diapers and Towels

Sub-strate	No. of items sampled	No. of samples per item	Average residual surfactant ppm	Estimated standard deviation, ppm		
				Between items	Within items	Of average residual surfactant
D	5	2	705	36.7	28.0	18.7
T	5	2	628	32.1	27.9	16.7
D	5	2	741	62.6	21.3	28.8
T	5	2	768	92.4	27.4	42.1

Adsorption Studies

For a more precise comparison of the surfactants, several adsorption studies were run under conditions more carefully controlled than is possible in a washing machine. All conditions of temperature, water hardness, inorganic builder, and cloth to solution ratio were the same as in the rinsability studies. One hundred milliliters of the appropriate aqueous solutions of surfactant and builders were placed in stoppered 250 ml Erlenmeyer flasks and a 5.3 g swatch of scoured diaper was placed in each. Aliquots were withdrawn and analyzed by liquid scintillation counting (1). The quantity of surfactant on the cotton was then obtained by difference. For other than the rate studies, the flasks were held for about 24 hr before sampling to ensure equilibrium. Occasional shaking ensured good mixing.

The first set of isotherms was obtained using the LAS, the C_{14}–C_{15}, and C_{12}–C_{15} sulfates, all S^{35} labelled. The data are presented in Figure 2 and resemble conventional adsorption isotherms having an

TABLE IV

Rinsability of a Surfactant Containing Na C_{14}–C_{15} Sulfate/Na Alkylbenzene Sulfonate (50/50)

Wash number	Water hardness, ppm	Soil	Sub-strate	Residual Surfactant, ppm		
				Alkyl sulfate[a]	LAS[b]	Total
1	140–150	Sebum	D	623	706	1329
			T	491	589	1080
2	140–150	Sebum	D	702	818	1520
			T	496	608	1104

[a] S^{35}-labelled.
[b] H^3-labelled.

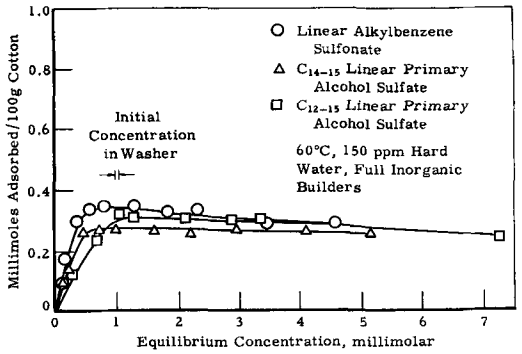

FIG. 2. Adsorption isotherms of sulfonates and sulfates.

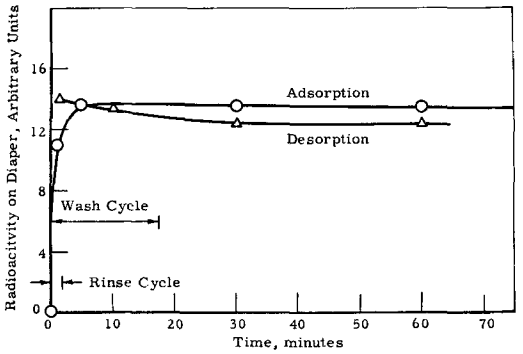

FIG. 3. Adsorption and desorption rates of C_{12}–C_{15} sulfate.

initial steep rise followed by a plateau. The exception to this seems to be the slow decline in concentration of adsorbed LAS with increasing equilibrium concentration in the solution. This has been attributed to the displacement of adsorbed monomer by micelles at the higher concentrations (10). One should note that in this system the pronounced maxima reported by others do not appear (3,4).

It is also of interest to compare these data with the rinsability data. The initial concentration of the surfactants in the washing machine experiments was 0.4 g/liter. Since, in the rinsability studies, roughly 10% of the surfactant is adsorbed by the diaper, the final solution concentration of each surfactant in the washing machine was about 0.36 g/liter. The C_{12}–C_{15} sulfate has an average molecular weight of 309, thus the solution is 1.16 mM. At this concentration one finds 0.31 mM absorbed/100 g cotton at equilibrium (see Fig. 2). Translating this into ppm for comparison, one obtains 958 ppm, in excellent agreement with 965 ppm for this surfactant in the rinsability study (Table II). Comparable calculation for the LAS shows 1215 ppm from the adsorption isotherm and 1266 ppm in the rinsability study. This agreement suggests that the rate of adsorption must be fast compared to the 20 min washing cycle in the machine to allow such an approach to equilibrium and that the desorption rate must be slow compared to the rinse cycle. Figure 3 presents a time study of adsorption and desorption which clearly supports the above statement. The desorption experiment was run in hard water (150 ppm) only, using the same procedure as in the adsorption experiment. One may also conclude that a few simple flask experiments can supply needed rinsability data, thereby avoiding the more tedious washer-dryer runs.

The effect of alcohol on the adsorption isotherms is also of interest. Figure 4 presents three isotherms obtained with the C_{12}–C_{15} sulfate in the presence of increasing alcohol content. It is clear that at 10.7% free detergent-range (C_{12}–C_{15}) alcohol, the isotherm is quite different from those at the lower concentrations. The reason for this effect is believed to be the same as that advanced above for the rinsability results in Table V, namely, an insoluble alcohol/surfactant complex which deposits more easily on the surface. However, even in such a complex system the adsorption isotherm (10.7%, Fig. 4) can again be used to approximate the rinsability values. In this case the isotherm predicts, at 1.16 mM equilibrium concentration, 1370 ppm residue and one finds (8.3% alcohol, Table V) about 1400 ppm.

If, as is shown above, the isotherms can be used to predict rinsability data, then the effect of free alcohol on rinsability over a very wide range can be obtained by running a series of flask experiments, as was done for the isotherms. This was done at a surfactant concentration of 0.4 g/liter (as in the washer) plus other similar conditions (i.e., cotton, hardness, temperature, builder) but the free alcohol concentration was varied. The samples were held for 24 hr, with occasional shaking to ensure equilibrium and then were sampled and counted. The concentration of surfactant on the cloth was obtained by difference (from the original count) and the plot is shown in Figure 5. The data are expressed in ppm on the cloth for ready application to rinsability performance.

This plot demonstrates that alcohol indeed has an effect on surfactant retention. The slight dip at 7% is a real effect showing up in repeat runs. The cause of this is not known. However, one can readily obtain, from Figure 5, the expected retention from alcohol sulfates of different free alcohol content. Furthermore, a maximum is reached at about 22% free alcohol (2000 ppm) which slowly declines with increasing concentration. Concentrations of alcohol at these levels are not likely to be encountered in commercial preparations.

The values of the rinsability and adsorptivity studies may be affected by the presence of wax on the cotton as shown by Ginn et al. (12) and thus may not be representative of pure cotton.

TABLE V
Effect of Free Alcohol on Rinsability

Detergent	% Free alcohol	Substrate	Residual surfactant, ppm			
			1[a]	2	3	4
C_{14}–C_{15} sulfate[b]	1.1	D	1120	1252	.....	.....
		T	1041	1126	.....	.....
C_{12}–C_{15} sulfate	3.3	D	929	1002	.....	.....
		T	859	912	.....	.....
C_{12}–C_{15} sulfate	8.3	D	896	1097	1427	1365
		T	859	982	1160	1323
C_{12}–C_{15} sulfate	13.3	D	956	1339	.....	.....
		T	944	1286	.....	.....

[a] Wash number.
[b] From Table II.

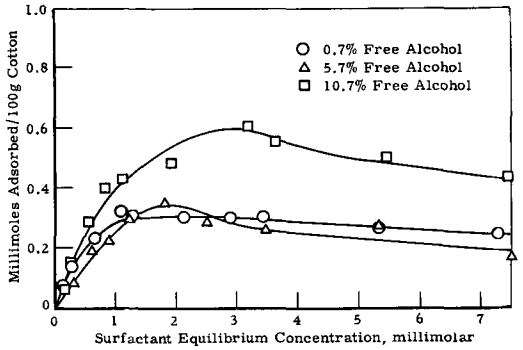

FIG. 4. Effect of free alcohol on adsorption isotherms (C_{12}–C_{15} sulfate).

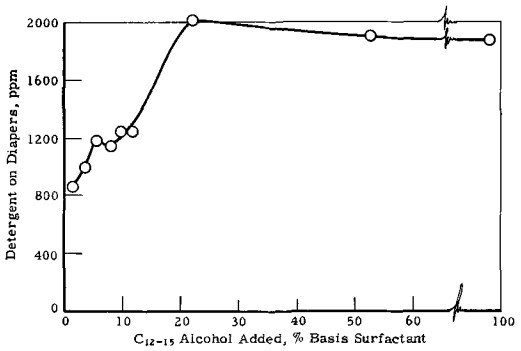

FIG. 5. Effect of C_{12}–C_{15} alcohol on adsorption of surfactant.

Residues of linear, primary alcohol sulfates and linear alkylbenzene sulfonates left on cotton substrate after a washer-dryer cycle are comparable, with those of the sulfates being slightly lower. Equilibrium concentrations of these residues are reached after the first cycle. Fifty/fifty mixtures of alcohol sulfates and alkylbenzene sulfonates leave residues not significantly different from that which could be expected from the unmixed residues; i.e., the residue is composed of about equal parts of each surfactant and the total is the same as that from unmixed surfactant rinsability studies. Free detergent-range alcohol increases the residue concentration in a rinsability test only when it exceeds about 8% w basis surfactant. Even at 10.7% free alcohol the increase is nominal going from about 1000 ppm (0.10%) to about 1300 ppm (0.13%) after two cycles. Rinsability experiments using non-radioactive linear, primary alcohol sulfates to wash cotton fabrics containing equilibrium concentrations of this radioactive surfactant show rapid and extensive exchange indicating that the surfactant is present in a reversibly adsorbed state. The presence of soil (sebum) has little effect on the residue concentration of either sulfate or sulfonate.

Adsorption studies demonstrate that both sulfates and sulfonate yield isotherms having a rapid initial rise followed by a plateau, under conditions of temperature, water hardness, and builders similar to those in the rinsability tests. The adsorption isotherms can be used to predict rinsability (residue) performance in a conventional washer-dryer cycle because the rate of adsorption is fast compared to the 20 min wash cycle used and the rate of desorption is slow compared to the 2 min rinse cycle.

Free alcohol increases the concentration of C_{12}–C_{15} sulfate on cotton but not significantly until one reaches somewhere between 5.7 and 10.7% free alcohol, basis surfactant. This effect may be due to the formation of an insoluble alcohol/alkyl sulfate complex.

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