A Quantitative Study of Factors That Influence the Substantivity of Fragrance Chemicals on Laundered and Dried Fabrics

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Model investigations of physicochemical aspects of the substantivity of fragrance raw materials on laundered fabrics were performed. The overall process was divided into two consecutive steps, laundry and dryout, which were characterized by affinity and tenacity, respectively. The affinities of fifteen fragrance raw materials to cotton and polyacrylonitrile were measured in standard fabric softener and detergent solutions. Affinities correlated with the corresponding partition coefficient, P(o/w). To study the impact of parameters independent of the chemical structure of the fragrance molecules, 1-[³H]-3-methyl-5-phenylpentanol (phenylhexanol) was selected, and aqueous solutions of defined anionic, nonionic and cationic surfactants were used as model detergent and fabric softener media. A sequence of experiments, based on the fractional factorial design, was planned for quantifying the relative contribution on substantivity of a number of variables: the concentration of the fragrance chemical, the type and concentration of the surfactants, the type and weight of the fabrics (cotton or polyacrylonitrile) and the washing temperature in the case of cotton. The affinity that characterizes the washing process depends mainly on the type of fabric and the type of surfactant and, to a lesser extent, on the surfactant concentration and the temperature. Anionic and nonionic surfactants, the main components of detergent powders, behave similarly, whereas the combination of cationic surfactant with cotton markedly enhances the affinity. For phenylhexanol, the tenacity after dryout is largely controlled by the type of fabric. The role of fiber swelling is discussed. The substantivity, which represents the global effect of laundering and dryout, shows the same trend as the affinity. The complexity of the physicochemical phenomena involved is highlighted by the importance of the interactions between the main contributing factors.

KEY WORDS: Affinity, fractional factorial design, fragrance raw material, hydrophobicity, influencing factors, laundered and dried fabrics, quantification, substantivity, surfactants, tenacity.

The laundry process regenerates a clean and fresh appeal to clothes and fabric materials. Detergent systems are designed to remove organic and inorganic dirty matter, whereas the fragrance, which by itself is a blend of organic compounds, is expected to be transferred from the same system to the fabric and to be gradually released during the dryout and subsequent storing of the laundered material. A long-lasting odor, slowly emitted from the laundered fabric, is a desired property of detergent perfumes, which is often described as substantivity and tenacity (1–4). Sturm and Mansfeld (1) studied the residuality of fragrance

chemicals on fabric that was laundered with nonperfumed detergent powder and then treated with a perfumed softener in the final rinsing. The amount of fragrance chemicals extracted from the fabric processed in this manner was correlated with the gas-liquid chromatographic retention times, the functional groups and the odor characteristics of the individual compounds, as well as with the fabric type. Practical, useful conclusions were drawn. However, no explanation of the results was offered on a physicochemical basis. The investigation of more than 250 fragrance raw materials in fabric softener application by means of olfactory evaluation on fabric was reported by Jellinek and Warnecke (2). The type and concentration of cationic softener agents had little impact on the adsorption of perfume chemicals on mixed cotton–polyester fabric. The amount of perfume chemicals in the solvent extracts of the rinsed fabrics (measured by means of spectrophotometry) was proportional to the concentration of these chemicals in the softener rinse liquor. The adsorption of perfume chemicals to surfactant micelles was discussed, and it was suggested that the adsorption of surfactant and perfume on the fabric go parallel. Etzweiler et al. (3) used quantitative headspace techniques to investigate stability and substantivity of perfumes. Recently, Neuner-Jehle and Etzweiler (4) and Müller et al. (5) have combined these methods with olfactometric techniques to provide a useful tool for objectively quantifying the perceived substantivity of fragrance chemicals in detergent application. From a large body of data, a number of important factors emerged that have a marked influence on substantivity of fragrance chemicals in laundry (4), e.g., the presence of special functional groups in the perfume chemicals and the nature of the fabric; however, details were not disclosed. Interaction of fragrance chemicals with products, such as detergent powders or fabric softeners, was characterized by an experimentally determined factor (4,5). The authors concluded (5) that a fragrance chemical can be regarded as substantive if it has the following properties: a medium-to-low vapor pressure, a low odor threshold and a polarity that favors release from the product.

The knowledge of the fate of the fragrance raw materials (FRM) in detergent application is of great interest in functional perfumery, and the aim of the present study is to identify and to quantitate factors pertinent to the substantivity of fragrance chemicals on laundered and dried fabrics. The study does not implement olfactory considerations, e.g., the detection thresholds, the odor quality and strengths of the fragrance chemicals in question, but is devoted to the investigation of physicochemical aspects that underlie substantivity.

Preliminary studies (see Experimental Procedures section) of the behavior of fifteen tritium- or ¹⁴C-labeled FRM in detergent and fabric softener applications with a model apparatus demonstrated that the hydrophobicity of the FRM [expressed as partition coefficient, P(o/w) (6,7)] plays an important role. This property depends on the molecular structure of the chemicals (7).

Important "external" factors identified include the surfactant system and the fabric. The present study emphasizes

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TABLE 1

Hydrophobicity [logP(o/w)] and Affinity [log(y_a)] to Fabric of 15 Fragrance Raw
Materials in Model Laundry Applications[a]

Fragrance raw material	LogP(o/w)	Affinity [log(y_a)]			
		S-C	S-A	D-C	D-A
Phenethyl alcohol	1.333	−1.327	−1.443	−1.346	−1.468
Lyral®	1.791	−1.143	−1.347	−1.229	−1.444
Ethyl vanilline	1.799	−0.557	−0.747	−1.327	−1.456
Hedione®	2.319	−1.013	−1.161	−1.408	−1.508
Citronellol	3.013	−0.669	−1.142	−1.092	−1.495
Lilial®	3.250	0.152	−0.503	−0.747	−1.102
Phenylhexanol	3.319	−0.554	−0.951	−1.045	−1.292
Mayol®	3.330	−0.268	−0.866	−1.022	−1.337
α-Ionone	3.740	−0.413	−0.672	−0.764	−0.987
Benzyl salicylate	4.383	0.689	−0.313	−1.086	−1.309
2-Amylcinnamaldehyde	4.445	0.755	−0.077	−0.439	−0.721
Polysantol®	4.490	0.833	−0.399	−0.590	−0.966
2-Hexylcinnamaldehyde	4.974	1.340	0.036	−0.416	−0.577
Ambrox®	5.270	0.775	−0.245	−0.433	−0.962
Norlimbanol®	5.870	1.246	−0.312	−0.529	−0.838

[a]Detergent (D) and fabric softener (S) concentrations at 0.5%; test fabrics, cotton (C) and
polyacrylonitrile (A); laundry temperature, 30°C.

the quantitation of the relative influence of selected variables on substantivity, namely nature and concentration of the surfactants, type and load of the fabrics (cotton and polyacrylonitrile), the fragrance concentration and the washing temperature. A sequence of sets of experiments was planned in the form of fractional factorial matrices, by using the Methodology of Optimal Experimental Design (8–10). For this part of the study, tritiated phenylhexanol (PH) (1-[³H]-3-methyl-5-phenylpentanol) was selected as a representative fragrance chemical. This chemical is sufficiently hydrophobic to show good affinity to cotton and polyacrylonitrile, and its volatility is sufficiently low to prevent total loss during dryout on fabric. The experimental region was defined according to preliminary experiments. Solutions of single anionic, cationic or nonionic surfactants were applied as model detergent and softener media, and the laundry step was performed, as above, in a model apparatus.

The overall process was divided into two consecutive steps, laundry and dryout, which were characterized by affinity and tenacity, respectively. The affinity was assigned to the laundry step and was defined as the partition coefficient of PH (or FRM for Table 1) between the fabric and the wash liquor. The tenacity was defined as the ratio of the amount of PH on the dry, as opposed to the wet, fabric. The substantivity was attributed to the residuality of PH on the fabric after the overall process.

EXPERIMENTAL PROCEDURES

Standard bleached cotton fabric (percale, no optical brightener, 90 g/m²) and polyacrylonitrile fabric (orlon type 75, 150 g/m²) were purchased from the Swiss Federal Laboratories for Materials Testing and Research (St. Gallen, Switzerland). The detergent powder was ECE Color Fastness Test Detergent 77 (Henkel, Düsseldorf, Germany). The fabric softener was 5% ARQUAD 2HT-75 (AKZO, Düren, Germany). These standard formulae were used at 0.5% concentration. Single surfactants were used as purchased: Cetyltrimethylammonium bromide (CTAB) [purum, critical micelle concentration (CMC) = 9.2×10^{-4} mol/L (11); Fluka, Buchs, Switzerland]; sodium dodecyl sulfate (SDS)

[puriss., CMC = 8.3×10^{-3} mol/L (11); Fluka]; Triton-X100 (TX) [CMC = 2.7×10^{-4} mol/L (12), molecular formula $C_{33}H_{60}O_{10.5}$; Fluka]. The surfactant solutions were prepared with tap water; the water hardness was 131 ppm $CaCO_3$ (=13.1°U.S.). Radiolabeled FRM were synthesized from suitable precursors with sodium cyanoboro[³H]hydride or [¹⁴C]-methyl iodide (Amersham, United Kingdom). The crude reaction products were purified to constant specific activity by successive liquid–liquid and gas–liquid chromatographic separations. The compounds were stored in pentane solution at 0°C. Appropriate aliquots were concentrated and diluted with n-butanol prior to application.

Tritium and carbon-14 were measured at a 2% 2σ confidence level on fabric and in surfactant solution by liquid scintillation counting (LSC) with a Beckman counter. (model 3801; Beckman Instruments, Nyon, Switzerland). Glass vials (22 mL) were obtained from Canberra Packard (Zurich, Switzerland). The cocktail consisted of 10 mL of a mixture of ReadySolv®HP (Beckman) water, (9:1, vol/vol) for both the fabric and the sample solutions in toluene (vide infra) and of 9 mL of ReadySolv®HP for the aqueous samples. The quench curves were established with ReadySolv®HP water (9:1, vol/vol). The volume of the aliquots of both the aqueous and the toluene samples (vide infra) was 1.0 mL. The weight of the fabric aliquots was 0.2–0.3 g.

Each experiment was triplicated. Typically, surfactant solution (20.0 g = 20 mL) was added to 3 × 3 22-mL glass vials equipped with aluminum foil-lined screw caps, and 20 mL toluene was added to 1 × 3 vials. Exactly weighed fabric swatches were placed into 2 × 3 of the surfactant vials, the remaining 3 vials being used for a control experiment (vide infra). Labeled PH (or FRM, in the case of Table 1) in n-butanol (10 µL, 5×10^5 dpm) and 20 µL of a solution containing 50 or 100 mg of PH (FRM) in 10 mL of n-butanol was dispensed to each of the 12 vials. Two 1-mL aliquots of each of the three toluene solutions were measured by LSC [100% PH (FRM)]. The nine surfactant-containing vials were stacked horizontally into a damper-lined jar, and the jar was fixed on a
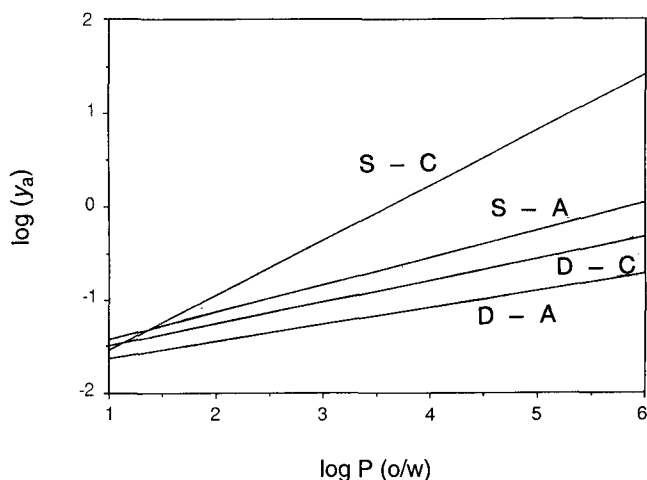
FIG. 1. Hydrophobicity [logP(o/w)] vs. affinity [log(y_a)] of 15 FRM (see Table 1 for abbreviations). S-C: $y = -2.18 + 0.61x$ ($R^2 = 0.87$); S-A: $y = -1.72 + 0.29x$ ($R^2 = 0.74$); D-C: $y = -1.72 + 0.23x$ ($R^2 = 0.77$); D-A: $y = -1.82 + 0.18x$ ($R^2 = 0.67$).

thermostated shake table (30 or 60°C) and agitated at 200 rpm. After the equilibrium had been reached (one night), two 1-mL aliquots each out of three of the surfactant solutions that contained fabric were assayed by LSC [→%PH (FRM) in the wash liquor]. Two 1-mL aliquots each of the three surfactant samples devoid of fabric were also measured. Within the experimental error, these values corresponded to 100% PH (FRM), showing that the PH (FRM) was fully soluble in the surfactant media employed. The surfactant solutions were sucked away by means of a pipette connected to a water jet pump, and the 2 × 3 swatches were quickly centrifuged. The weight increase of the wet fabrics due to retained surfactant liquor was 7% for cotton and 3% for polyacrylonitrile. Three of the swatches were cut into 3–4 sub-swatches, which were assayed by LSC [→%PH (FRM) on wet fabric]. The three remaining swatches were placed in a ventilated dryer that was thermostated at 40°C and assayed by LSC after 2 h [→%PH on dry fabric]. Calculations for:

affinity:

$$y_a(\%) = (\%\text{PH}_{\text{on wet fabric}}/\%\text{PH}_{\text{in wash liquor}}) \times 100 \qquad [1]$$

tenacity:

$$y_t(\%) = (\%\text{PH}_{\text{on dry fabric}}/\%\text{PH}_{\text{on wet fabric}}) \times 100 \qquad [2]$$

substantivity:

$$y_s(\%) = [\%\text{PH}_{\text{on dry fabric}}/(\%\text{PH}_{\text{on wet fabric}} + \%\text{PH}_{\text{in wash liquor}})] \times 100 \qquad [3]$$

The partition coefficient octanol/water [P(o/w)] of the FRM was retrieved from tables (6) or calculated by the Hansch fragmentation method (6). Affinity y_a for the FRM was calculated from the experimental data as shown for PH. Log(y_a) was then plotted against logP(o/w) (Table 1 and Fig. 1).

EXPERIMENTAL DESIGN

Methodology. The quantitation of the influence of different experimental factors (or independent variables, which can be controlled by the experimenter) on a given process can be made easier and more effective by using proper methodology, especially if many factors are likely to affect the process. The method that consists of changing the level (setting or value) of one variable at a time, while maintaining the other variables at fixed levels, is inappropriate for several reasons (13): (i) The number of experiments to be carried out rapidly becomes very large; (ii) this procedure will fail in most cases if the factors studied are not intrinsically independent, *i.e.*, if the effect of a given factor depends on the setting of another factor, *vice versa*; (iii) conclusions drawn from such experiments may be completely misleading, as they do not give any information on how such interactions affect the process. Efficient experimental designs, based on multivariate methods and adapted to various types of problems, have been proposed for quite some time (8,14,15). Among them, complete and fractional factorial designs (8,16,17) allow the quantitation of the main effects of, and the interactions between, several factors. With this type of design, experiments may be performed in sequential steps, and the information acquired from a series of experiments can be used to more adequately plan the next step. Before choosing the most appropriate set of experiments or sequence of several experimental sets, the responses of interest, which are assumed to be affected by changing the settings of the factors, must be defined. The experimental region of interest, *i.e.*, range of variation of the levels of the different factors, must be determined. The reproducibility of the experiments must be checked. Some factors can be defined by several variables, the factor "surfactant" being, for instance, characterized by the two variables "type" and "concentration".

Responses, factors, experimental region. The methodology outlined above was applied to the study of the effects of several factors on the substantivity of a fragrance chemical on fabrics. The experimental procedures (*vide supra*) for measuring the responses of interest, affinity [denoted $y_a(\%)$, laundry step] and tenacity [denoted $y_t(\%)$, dryout] were established by preliminary experiments with PH as FRM. The third response, substantivity, measured as the level of PH on the dry fabric [$y_s(\%)$], represents the global effect of laundry followed by dryout.

The factors likely to influence the substantivity and their range of variation (experimental region) were selected on the basis of the experiments with the FRMs and standard detergent and fabric softener formulations. In these experiments, we observed large variations in the affinity between treatments with detergent and with fabric softener (Table 1). Supposedly, the main cause was the different nature of the surfactants contained in detergent powders (anionic and nonionic) and fabric softeners (cationic), and we decided to test each type of surfactant separately. The six variables investigated and their ranges of variation are as follows:

Variable 1, concentration of surfactant ([SU]): minimum value, 5.0×10^{-4} mol/L (< CMC of the ionic surfactants); maximum value 1.0×10^{-2} mol/L (> CMC). Variable 2, concentration of PH ([PH]), minimum value, 100 µg; and

maximum value, 200 μg per 20 g of surfactant solution, which is a realistic range from a practical point of view. Variable 3, type of surfactant (SU): SDS as an anionic, CTAB as a cationic and TX as a nonionic surfactant. Variable 4, type of fabric (F): polyacrylonitrile (A) and cotton (C). Variable 5, weight of fabric ([F]): minimum value, 0.75 g and maximum value, 1.00 g per 20 g of surfactant solution. In the case of cotton fabric, the effect of the washing temperature (T, variable 6), minimum value, 30°C; and maximum value, 60°C; was also investigated.

As the different natural variables are expressed in different units and are of qualitative (type of fabric, type of surfactant) or of quantitative character, their effects can only be compared if they are coded or scaled (see *Experimental matrices*).

Experimental matrices. The objective of the experimentation was to determine which of the six variables listed above were of decisive importance, and to quantify their effects and their eventual interactions. A sequential approach (10) was used. Four successive experimental matrices were designed, comprising a total of 30 different experiments. Several of these experiments were repeated to check the reproducibility and to test conclusions derived from the different steps of the experimentation. The matrices chosen were based on fractional factorial designs (17), with the variables set at two different levels, corresponding to the limits of the experimental region, and coded (−1) and (+1).

Complete factorial designs 2^k allow the determination of the main effects of k variables, as well as of all their mutual interactions from first-order (between 2 variables) to (k−1)-order (between k variables). They require a minimum of 2^k experiments, which correspond to all possible combinations of the k variables set at the two levels coded, (−1) and (+1). However, the number of experiments can be considerably reduced because, in general, higher-order

interactions, and even some first-order interactions (between two variables), can be assumed to be zero or negligible. In such a case, fractional factorial designs 2^{k-p} can be used. Formally, factorial matrices are associated to a response function y, which is represented when only first-order interactions are taken into account by a polynomial model of the form:

$$y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ij} X_i X_j \qquad [4]$$

where i ≠ j, X_i, X_j = coded variables i and j [(−1) or (+1)]; b_0 = average value of the experimental responses; b_i = main effect of variable i; and b_{ij} = first-order interaction between variables i and j.

The experimental matrix corresponding to a given design determines the settings of the variables [(−1) or (+1)] for each experiment. Once the series of experiments has been carried out, estimates of the coefficients b are calculated from the observed response values y, by using regression and least squares methods for fitting the data (18). Note that the coefficients are expressed in the same units as the responses. In fact, in the case of a 2^{k-p} fractional factorial matrix, 2^{k-p} coefficients (denoted L) can be calculated. These coefficients are strictly equal to the sum of two or several coefficients b (main effects and/or interactions of various orders), depending on the value of p and on the choice of the experimental matrix. Thus, the estimate of a given coefficient b will only be correct if the hypotheses made on the insignificance of the other coefficients b in the corresponding sum L are correct.

A 2^{5-1} fractional factorial matrix was designed for comparing the two surfactants SDS and CTAB at the same temperature (30°C). This matrix, containing 16 experiments, was used for the quantitation of the effects of variables 1–5 (matrix A, Table 2).

TABLE 2

Experimental Matrix 2^{5-1} (matrix A) in Natural Variables, and Values of the Responses[a]

Experiment	1 [SU]	2 [PH]	3 SU	4 F	5 [F]	y_a (%)	y_t (%)	y_s (%)
1	min	min	SDS	A	max	5.9	6.7	0.4
2	max	min	SDS	A	min	3.0	10.0	0.3
3	min	max	SDS	A	min	4.2	9.8	0.4
4	max	max	SDS	A	max	4.7	6.4	0.3
5	min	min	CTAB	A	min	6.1	8.5	0.5
6	max	min	CTAB	A	max	3.1	20.0	0.6
7	min	max	CTAB	A	max	8.1	8.0	0.6
8	max	max	CTAB	A	min	3.3	15.6	0.5
9	min	min	SDS	C	min	7.2	86.9	5.9
10	max	min	SDS	C	max	8.5	83.1	6.6
11	min	max	SDS	C	max	10.0	80.0	7.3
12	max	max	SDS	C	min	7.7	80.0	5.7
	max	max	SDS	C	min	6.2	85.0	5.0
	max	max	SDS	C	min	5.8	91.2	5.0
	max	max	SDS	C	min	6.2	86.4	5.0
13	min	min	CTAB	C	max	32.6	93.8	23.0
14	max	min	CTAB	C	min	12.1	90.2	9.7
15	min	max	CTAB	C	min	29.8	94.8	21.8
16	max	max	CTAB	C	max	15.3	92.3	12.3

[a]The values are to evaluate the relative influence of the type and concentration of surfactant (anionic and cationic), the type and weight of fabric and the fragrance (PH) concentration on affinity (y_a), tenacity (y_t) and substantivity (y_s) {the coded matrix used for the calculations can be obtained from the following codes: [SU], [PH] and [F], min (−1) and max (+1); SU, SDS (−1) and CTAB (+1); F, A (−1) and C (+1)}. Abbreviations: PH, phenylhexanol; [SU], concentration of surfactant (SU); [PH], concentration of PH; [F], weight of fabric (F); SDS, sodium dodecyl sulfate; CTAB, cetyltrimethylammonium; A, polyacrylonitrile; C, cotton.

TABLE 3

Experimental Matrix 2^{5-1} (matrix B) in Natural Variables, and Values of the Responses[a]

Experiment	1 [SU]	2 [PH]	3 SU	4 T	5 [F]	y_a (%)	y_t (%)	y_s (%)
9^b (1)	min	min	SDS	30°C	min	7.2	86.9	5.9
12^b (2)	max	max	SDS	30°C	min	7.7	80.0	5.7
15^b (3)	min	max	CTAB	30°C	min	29.8	94.8	21.8
14^b (4)	max	min	CTAB	30°C	min	12.1	90.1	9.7
11^b (5)	min	max	SDS	30°C	max	10.0	80.0	7.3
10^b (6)	max	min	SDS	30°C	max	8.5	83.1	6.6
13^b (7)	min	min	CTAB	30°C	max	32.6	93.8	23.0
16^b (8)	max	max	CTAB	30°C	max	15.3	92.3	12.3
17 (9)	min	min	SDS	60°C	min	6.1	83.0	4.7
18 (10)	max	max	SDS	60°C	min	4.8	95.8	4.4
19 (11)	min	max	STAB	60°C	min	20.2	92.8	15.6
20 (12)	max	min	CTAB	60°C	min	8.9	90.9	7.4
21 (13)	min	max	SDS	60°C	max	7.9	77.8	5.7
22 (14)	max	min	SDS	60°C	max	6.3	86.1	5.1
23 (15)	min	min	CTAB	60°C	max	23.4	94.9	18.0
24 (16)	max	max	CTAB	60°C	max	12.3	91.1	10.0

[a]The values are to evaluate the relative influence of the type and concentration of surfactant (anionic and cationic), the weight of fabric and the temperature on affinity (y_a), tenacity (y_t) and substantivity (y_s) in the case of cotton {the coded matrix used for the calculations can be obtained from the following codes: [SU], [PH] and [F], min (−1) and max (+1); SU, SDS (−1) and CTAB (+1); T, 30°C (−1) and 60°C (+1)}. Abbreviations as in Table 2. T, temperature.
[b]Experiments from matrix A (Table 2).

With such a matrix, 16 coefficients L (taking into account only first- and second-order interactions) may be calculated from the experimental results, for each response of interest: $L0 = b_0$; $L1 = b_1$; $L2 = b_2$; $L3 = b_{12}$ (+ b_{345}); $L4 = b_3$; $L5 = b_{13}$ (+ b_{245}); $L6 = b_{23}$ (+ b_{145}); $L7 = b_{45}$ (+ b_{123}); $L8 = b_4$; $L9 = b_{14}$ (+ b_{235}); $L10 = b_{24}$ (+ b_{135}); $L11 = b_{35}$ (+ b_{124}); $L12 = b_{34}$ (+ b_{125}); $L13 = b_{25}$ (+ b_{134}); $L14 = b_{15}$ (+ b_{234}); $L15 = b_5$. L_0 (b_0) is the average value of a given response for the 16 experiments. The main effects, b_1 to b_5, can be calculated independently from interaction effects. First-order interactions are obtained independently, provided that second-order interactions (listed in parentheses) are negligible. However, in general, the latter are only significant if the three corresponding first-order interactions are themselves important.

A second 2^{5-1} factorial matrix was designed for determining the relative influence of temperature (variable 6) in cotton. Matrix B (Table 3) is similar to matrix A (Table 2). As a matter of fact, the eight experiments already performed with cotton at 30°C for matrix A were included in matrix B, and eight additional experiments were carried out at 60°C.

The results from matrices A and B were analyzed (see Results section), and additional experiments were planned to compare SDS and TX, as well as TX and CTAB. Because we could show from the results of matrices A and B that variable 2 had a negligible effect on the substantivity, only 4 variables (1, 3, 4 and 5) were studied in the next step of the investigation. Matrices representing 3/4 of a 2^4 complete factorial design were used. Such matrices include 12 experiments and can be divided into three 2^{4-2} fractional factorial submatrices. The coefficients L calculated from the experimental results of these submatrices are combined in half-sums and half-differences, respectively, for independently evaluating the interactions of interest, assuming that, in agreement with the results from matrices A and B, the interactions b_{1345}, b_{145}, b_{345} and b_{15} are negligible. Matrix C was designed

for comparing anionic and nonionic surfactants (SDS and TX). Among the 12 experiments planned, 6 had already been performed for matrix A, but were repeated (Table 4). Matrix D, similar to matrix C, was used for comparing CTAB and TX; no additional experiments had to be carried out for this matrix (Table 5).

RESULTS

Effects of different factors on the affinity (comparison SDS-CTAB. Mathematical treatment of the values of the response y_a for matrix A (Table 2) gives the estimates for the effects of variables 1 to 5 ([SU], [PH], SU, F and [F]) on the affinity of PH in the case of the comparison SDS-CTAB. The standard deviation of y_a was calculated to be $s(y_a) = 0.8$ from the repetition of experiment No. 12. Among the 16 coefficients L calculated from matrix A, 6 coefficients ($L2$, $L3$, $L6$, $L10$, $L11$ and $L14$) are negligible, taking into account the experimental error. The standard deviation of coefficients L [$s(L)$] can be estimated in two independent ways—from the coefficients L that have negligible values, assuming that these values originate from random experimental errors, and from the experimental error $s(L) = s(y_a)/\sqrt{16}$. The two methods give the same value of $s(L)$, about 0.2.

Because $L2$ is equal to zero, the main effect b_2 (and its corresponding interactions) can be considered negligible, especially because coefficients L, including first-order interactions of variable 2 ($L3$, $L6$, $L10$) are also negligible (see *Experimental matrices* for the relations between b and L). Also, we can assume that, in the range studied, the fragrance concentration (variable 2) has no effect on the affinity. Four variables markedly affect the affinity (in decreasing order): the type of fiber ($b_4 = 5.2$) > the type of surfactant ($b_3 = 3.8$) > the concentration of surfactant ($b_1 = -3.0$) > the fabric weight ($b_5 = 1.0$). The values of these main effects, as well as those of the significant first- and second-order interactions (b_{13}, b_{14}, b_{34}, b_{45}

TABLE 4

Experimental Matrix (matrix C) in Natural Variables, and Values of the Responses[a]

Experiment	1 [SU]	2 [PH]	3 SU	4 F	5 [F]	y_a (%)	y_t (%)	y_s (%)
1 (1)	min	min	SDS	A	max	4.2	7.3	0.3
12[b] (2)	max	min	SDS	C	min	6.5	98.4	6.0
25 (3)	min	min	TX	A	min	3.8	8.1	0.3
26 (4)	max	min	TX	C	max	7.9	90.1	6.4
11[b] (5)	min	min	SDS	C	max	10.0	82.8	7.7
2[b] (6)	max	min	SDS	A	min	2.7	7.7	0.2
27 (7)	min	min	TX	C	min	9.5	90.9	8.0
28 (8)	max	min	TX	A	max	3.9	8.1	0.3
3[a] (9)	min	min	SDS	A	min	2.9	6.9	0.2
10[b] (10)	max	min	SDS	C	max	8.3	100.0	7.9
29 (11)	min	min	TX	A	max	4.2	4.9	0.2
30 (12)	max	min	TX	C	min	5.7	90.9	5.0

[a]The values are for the comparison of the effects of an anionic and a nonionic surfactant on affinity (y_a), tenacity (y_t) and substantivity (y_s) {the coded matrix used for the calculations can be obtained from the following codes: [SU], [PH] and [F], min (−1) and max (+1); SU, SDS (−1) and TX (+1); F, A (−1) and C (+1)}. Abbreviations as in Table 2. TX, Triton-X100.
[b]These experiments correspond to those of matrix A (Table 2), repeated with [PH] min.

TABLE 5

Experimental Matrix (matrix D) in Natural Variables, and Values of the Responses[a]

Experiment	1 [SU]	2 [PH]	3 SU	4 F	5 [F]	y_a (%)	y_t (%)	y_s (%)
7[b] (1)	min	max	CTAB	A	max	8.1	8.0	0.6
14[b] (2)	max	min	CTAB	C	min	12.1	90.2	10.1
25 (3)	min	min	TX	A	min	3.8	8.1	0.3
26 (4)	max	min	TX	C	max	7.9	90.1	6.4
13[b] (5)	min	max	CTAB	C	max	32.6	93.8	22.7
8[b] (6)	max	min	CTAB	A	min	3.3	15.6	0.5
27 (7)	min	min	TX	C	min	9.5	90.9	8.0
28 (8)	max	min	TX	A	max	3.9	8.1	0.3
5[b] (9)	min	min	CTAB	A	min	6.1	8.5	0.5
16[b] (10)	max	max	CTAB	C	max	15.3	92.3	12.3
29 (11)	min	min	TX	A	max	4.2	4.9	0.2
30 (12)	max	min	TX	C	min	5.7	90.9	5.0

[a]The values are for the comparison of the effects of a nonionic and a cationic surfactant on affinity (y_a), tenacity (y_t) and substantivity (y_s) {the coded matrix used for the calculations can be obtained from the following codes: [SU], [PH] and [F], min (−1) and max (+1); SU, CTAB (−1) and TX (+1); F, A (−1) and C (+1)}. Abbreviations as in Tables 2 and 4.
[b]Experiments from matrix A (Table 2).

and b_{134}), are listed in Table 6. The main effects b_3 and b_4 have positive values, which means, when taking into account the codes used (see Table 2), that the affinity on cotton is higher than on polyacrylonitrile and that the affinity in the presence of the cationic surfactant is higher than with the anionic one. However, variables **3** and **4** are not independent ($b_{34} = 3.4$). The affinity is higher on cotton for both surfactants (SDS and CTAB), but the difference in the affinity between polyacrylonitrile and cotton is larger for the cationic surfactant than for the anionic one. This situation is illustrated in Figure 2.

The concentration of surfactant (variable **1**) also significantly affects the affinity—b_1 is negative. We may conclude that the affinity is higher if [SU] is lower than the CMC. However, this effect is only important in the case of the cationic surfactant (interaction b_{13} negative) and is more noticeable with cotton than with polyacrylonitrile (interaction b_{14} is negative; Fig. 2). The value of the coefficient *L13* ($b_{25} + b_{134} = −1.7$) indicates that a second-order interaction between the three vari-

ables that most strongly influence the affinity (**1**, **3** and **4**) does exist; b_{25} being negligible (interaction between two variables that have no or little influence), $b_{134} \approx −1.7$. The effect of the fabric weight (**5**) is comparatively small ($b_5 = 1.0$), the affinity being only slightly improved by an increase of the fabric load (experiments 13 and 15; Table 2).

Optimal affinity is observed under the following conditions: cotton, cationic surfactant, surfactant concentration lower than the CMC, higher fabric load (experiment 13; Table 2).

Effects of different factors on the affinity (comparisons SDS-TX and TX-CTAB). Mathematical treatment of the values of response y_a for matrices C and D (Tables 4 and 5) gives the estimates of the effects of variables **1**, **3**, **4** and **5** ([SU], SU, F and [F]) on the affinity of PH, for comparisons SDS-TX and TX-CTAB. Variable **2** was omitted from the new experiments; [PH] = min was used. The standard deviation on coefficients *L* was estimated from the experimental error as about 0.23 [s(L) = s(y_a)/$\sqrt{12}$].

TABLE 6

Main and Interaction Effects of Variables 1-6 on Affinity (y_a) and Tenacity (y_t): Comparison Between Anionic, Cationic and Nonionic Surfactants[a]

	SDS–CTAB (−1)-(+1) (matrix A)		SDS–CTAB (−1)-(+1) (matrix B, cotton)		SDS–TX (−1)-(+1) (matrix C)		TX–CTAB (−1)-(+1)[b] (matrix D)	
	y_a	y_t	y_a	y_t	y_a	y_t	y_a	y_t
b_1	−3.0	0.0	−3.9	0.0	−0.8	≈0.0	−3.0	0.0
b_2	≈0.0	0.0	0.0	0.0	—	—	—	—
b_3	3.8	3.4	6.1	3.9	0.2	0.0	3.9	≈0.0
b_4	5.2	39.0	—	—	2.4	41.4	5.4	40.6
b_5	1.0	0.0	1.3	0.0	0.7	0.0	1.0	0.0
b_6	—	—	−2.0	0.0	—	—	—	—
b_{13}	−2.4	0.0	−3.3	−2.2	−0.3	0.0	−2.0	0.0
b_{14}	−1.7	≈0.0	—	—	−0.5	≈0.0	−2.2	≈0.0
b_{34}	3.4	0.0	—	—	0.0	0.0	3.0	0.0
b_{134}	−1.7	≈0.0	—	—	−0.3	≈0.0	−1.4	0.0
b_{45}	0.3	0.0	—	—	0.3	0.0	0.4	0.0
b_{16}	—	—	0.7	0.0	—	—	—	—
b_{36}	—	—	−1.1	0.0	—	—	—	—
b_{136}	—	—	0.8	0.0	—	—	—	—

[a]1, [SU]; 2, [PH]; 3, SU; 4, F; 5, [F]; 6, T. Abbreviations as in Tables 2 and 4.
[b]The signs (−1) and (+1) for TX-CTAB have been inverted relative to the experimental matrix D (Table 5), so that the cases SDS-CTAB and TX-CTAB could be compared directly. Indeed, the signs of the coefficients depend on the codes (−1) or (+1) of the two levels of the corresponding variables.
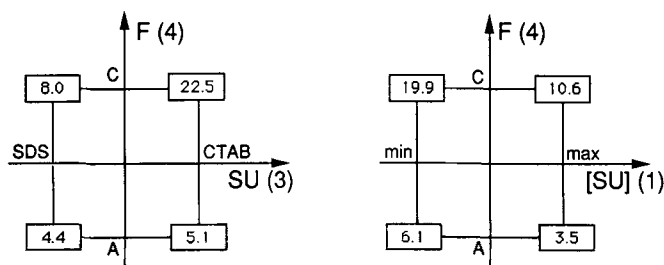

FIG. 2. First-order interactions between type of surfactant and type of fabric (b_{34}) and between concentration of surfactant and type of fabric (b_{14}) for affinity (y_a) in the case of the comparison SDS–CTAB (matrix A): average values of y_a in the four corresponding conditions are indicated on each graph (see Table 2 for abbreviations).

The values of main effects and interactions are listed in Table 6.

Taking into account the experimental errors, Table 6 shows that the anionic (SDS) and nonionic (TX) surfactants behave similarly. Indeed, close values of coefficients b have been obtained for the comparisons SDS–CTAB and TX–CTAB. Moreover, the direct comparison SDS–TX confirms that, the main effect of the nature of the surfactant (variable 3) is negligible [b_3(SDS-TX) = 0.2]. Therefore, the interaction effects related to variable 3 (b_{13}, b_{34} and b_{134}) are also negligible. On the contrary, changing the nature of the surfactant from nonionic to cationic (TX–CTAB), as well as from anionic to cationic (SDS–CTAB), markedly increases the affinity [b_3(SDS-CTAB) = 3.8, b_3(TX–CTAB) = 3.9], and the interactions involving variable 3 also have relatively large coefficients (Table 6).

Concerning variables 1, 4 and 5, similar results are obtained in all three cases (SDS-TX, SDS-CTAB, TX–

CTAB; Table 6). The variable that influences the affinity the most strongly is the type of fabric (4), the affinity on cotton being significantly higher than that on polyacrylonitrile. This can already be seen from the values of y_a in Tables 2, 4 and 5. The surfactant concentration (1) also plays a significant role in all three cases, but the ratio b_1/b_4 is smaller for SDS-TX. This result is in agreement with our previous observation (see *Comparison SDS-CTAB* section) that the effect of 1 is only important for the cationic surfactant.

The relative influence of the temperature on the affinity for cotton. Because variable 2 does not affect the affinity, we have 16 experiments at our disposal (matrix B, Table 3) for calculating the effects of 4 variables [1, 3(SDS-CTAB), 5 and 6]. These experiments belong to a 2^4 complete factorial matrix, and the main effects of, and all interactions between, the four variables may be evaluated (Table 6). As expected, all four variables influence the affinity. We again found the effects of the type of surfactant (3) and its concentration (1), a relatively smaller effect of the type of fabric (5), with absolute values of the corresponding coefficients being larger than for matrices including experiments with polyacrylonitrile, but with the same signs.

A temperature change from 30 to 60°C decreases the affinity (b_6 negative), and affects it more markedly than the fabric weight, but less than the surfactant (type and concentration). Interactions exist between temperature and surfactant. The second-order interaction (b_{136}) is relatively small, but nevertheless shows the complexity of the phenomenon.

By using matrix B, we could verify that the fragrance concentration (variable 2) has no effect on the affinity. The average of responses y_a for the eight experiments carried out with a minimum [PH] ($b_0^- = 13.1$) is equal, within experimental error, to the average of responses y_a for the eight experiments carried out with a maximum [PH] ($b_0^+ = 13.3$). There is no blocking effect.

TABLE 7

Main and Interaction Effects of Variables 1-6 on Substantivity (y_s): Comparison
Between Anionic, Cationic and Nonionic Surfactants[a]

$b(y_s)$	SDS-CTAB $(-1)-(+1)$ (matrix A)	SDS-CTAB $(-1)-(+1)$ (matrix B, cotton)	SDS-TX $(-1)-(+1)$ (matrix C)	TX-CTAB $(-1)-(+1)$[b] (matrix D)
b_1	−1.5	−2.6	−0.4	−1.7
b_2	0.0	0.0	—	—
b_3	2.7	4.6	≈0.0	−2.4
b_4	5.6	—	3.4	5.7
b_5	0.4	0.8	0.4	0.5
b_6	—	−1.3	—	—
b_{13}	−1.2	−2.3	−0.4	−1.0
b_{14}	−1.4	—	−0.4	−1.8
b_{34}	2.6	—	0.0	2.2
b_{134}	−1.3	—	−0.4	−1.0
b_{45}	0.4	—	0.4	0.5
b_{16}	—	0.4	—	—
b_{36}	—	−0.7	—	—
b_{136}	—	0.4	—	—

[a]Footnotes as in Table 6.

Effects of different factors on the tenacity. Similar to the case of affinity, mathematical treatment of the values of response y_t for matrices A-D (Tables 2-5) gives the estimates of the effects of variables 1-6 ([SU], [PH], SU, F, [F] and T for cotton) on the tenacity of PH. The standard deviation of y_t has been calculated (from repetition of experiment 12) to be $s(y_t) = 4.5$. The standard deviations of coefficients L_t for the tenacity [s(L_t) calculated from the experimental error $s(L_t) = s(y_t)/\sqrt{16} = 1.1$ for matrices A and B, and $s(y_t)/\sqrt{12} = 1.3$ for matrices C and D] are close to the values estimated from coefficients L_t which can be considered negligible, e.g., all coefficients except L_t0, L_t4 and L_t8 for the matrix A.

The tenacity of PH (after laundering and dryout) is much higher on cotton than on polyacrylonitrile (see values of y_t in Tables 2-5). In fact, the fabric type (4) has a dominant effect on the tenacity (Table 6). The main effect b_4 (=39.0) is 11 times higher than the next less important variable, namely the type of surfactant ($b_3 = 3.4$) in the case of comparison SDS-CTAB (Table 6). Although much smaller, b_3 is positive, showing a slightly better tenacity after laundering with the cationic surfactant. When TX and CTAB, or SDS and CTAB, are compared, the type of fabric appears to be the only influencing variable ($b_4 \approx 41$). In the case of cotton, the other variables [surfactant concentration (1), PH concentration (2), fabric weight (5), and temperature (6)] do not affect the tenacity. Interactions are negligible in the experimental region investigated. As for the affinity, no blocking effect due to the variation of the [PH] could be observed (b_0^+ = b_0^- = 89) for cotton (matrix B).

Effects of different factors on the substantivity. The mathematical treatment of the values of the response y_s for the matrices A-D (Tables 2-5) gives estimates for the effects of the variables 1-6 ([SU], [PH], SU, F, [F] and T for cotton) on the substantivity of PH. The standard deviation of coefficients L_s for the substantivity [s(L_s)] is about 0.1. The values of the main effects and the interactions for substantivity (Table 7), which represents the global effect of laundering and drying, show the same trend as the coefficients obtained for the affinity (Table

6). Tenacity appears, therefore, to play a secondary role in contributing to substantivity for a compound of low volatility such as PH, although a relative increase of the effect of fabric type (4), which controls the tenacity, is noticeable. In particular, coefficient b_4 is about eight times higher than the other effects for comparison SDS-TX. As in the previous cases (*vide supra*), no blocking effect due to variation of the concentration of PH could be observed (b_0^+ = 10.3, b_0^- = 10.1) for cotton (matrix B).

DISCUSSION

Our results on the affinity of PH with defined surfactants (anionic, cationic or nonionic) show that, among the factors investigated, the type of fabric (4) and the type of surfactant (3) are the main influencing variables, and that they are interdependent. The quantitation of their effects confirms the preliminary results obtained on a series of FRMs (Table 1) and shows that (i) irrespective of the hydrophobicity of the fragrance, affinity on cotton [which is more hydrophilic than synthetic fibers (19)] is higher than on polyacrylonitrile and (ii) a significant increase of the affinity is observed in changing from the treatment with a detergent formulation, which contains anionic and nonionic surfactants, to the use of a fabric softener, which contains only cationic surfactants, and the effect is enhanced for cotton. Therefore, the nature of the surfactants contained in detergent and softener formulations plays a dominant role in the affinity, and the other components have less impact.

The interaction effect between the type of fabric (4) and the type of surfactant (3) exemplifies the difference in behavior between a cationic surfactant and a nonionic or anionic one, with respect to cotton and polyacrylonitrile (Fig. 2). The affinity on polyacrylonitrile is rather low, and only weakly sensitive to the nature of the surfactant, whereas the affinity on cotton is higher and highly sensitive to the type of surfactant. Assuming that the surfactant plays a crucial part in the transport of the fragrance from the bulk solution onto the fiber (2), the large increase of the affinity for the combination cotton-

cationic surfactant could be due to more swelling of the cotton (more hydrophilic), which leads to a better penetration of both the surfactant and the fragrance into the fiber. There is also a specific interaction between cotton and the cationic surfactant, more pronounced than in the case of the other surfactants, thus limiting the redissolution of the surfactant and, therefore, of the fragrance. Experiments to investigate the adsorption of surfactants on various types of material have shown the complexity of the involved interactions (20–25). Surfactants induce modifications in the surface potential (ζ-potential) of fibers (22,23). On the one hand, adsorption of cationic surfactants on fabric is mainly controlled by electrostatic interactions, and the ζ-potential goes from a negative to a positive value as the surfactant concentration increases. On the other hand, anionic or nonionic surfactants should associate with fabric mainly through Van der Waals interactions. Adsorption phenomena also depend on pH (23), temperature (24), micellization [which, in turn, is influenced by additives, such as builders, and the temperature (24, 25)] and swelling, which modifies the fiber size (24).

The surfactant concentration (1) also significantly influences the affinity, and shows first-order and second-order interactions with the type of fabric (4) and surfactant (3) (Table 6). The affinity is higher when the surfactant concentration is lower than the CMC of the ionic surfactants, and this effect is only important in the case of CTAB and cotton. In fact, complementary experiments with cotton fabric have shown (Table 8 and Fig. 3) that a net maximum in affinity is observed when the concentration of the cationic surfactant approaches the CMC. This could be due to the particular relation between fabric weight and the concentration of CTAB, so that the surface charge of the fiber would be neutralized by the cationic surfactant. No clear maximum could be seen for SDS or TX (Fig. 3). In summary, the concentration of an anionic or a nonionic surfactant should have little influence on the affinity, whereas the concentration of a cationic surfactant should be rather low to improve affinity, and this is generally the case in fabric softener formulations.

The impact of the fabric weight (5, b_5) in the narrow range investigated is small, and comparable for the three types of surfactants. The interactions with other factors (b_{45}) are negligible. The effect of temperature (6) on the affinity (Table 6), analyzed in the case of cotton, is intermediate between the effects of fabric load and surfactant (type and concentration). An increase of temperature is unfavorable. This could be due to better solubility of PH at higher temperature. Interactions exist with the surfactant. They are relatively small and difficult to interpret.

The concentration of PH does not affect affinity, as could be expected considering that change of localization and distribution of the probe, which could influence the affinity, is improbable in the concentration range investigated (2.8 × 10^{-5} mol/L to 5.6 × 10^{-5} mol/L), namely concentrations that are much lower than the minimum surfactant concentration.

The tenacity of PH after laundering is largely controlled by the type of fabric (4). The role of fiber swelling, which determines the penetration and retention of the probe inside the fiber, is probably important in explaining both the higher tenacity and the higher affinity on cotton fabric.

TABLE 8

Experimental Data for Evaluating the Influence of Type and Concentration of Surfactant on Affinity (y_a) in the Region of the Critical Micelle Concentration (F, C; [F], max)^a

Experiment	1 [SU]^b	3 SU	y_a (%)
31	0.1	TX	8.5
32	0.5	TX	12.0
33	1.0	TX	13.8
34^c	10.0	TX	7.9
35^d	0.5	SDS	10.0
36	0.5	SDS	10.0
37^d	10.0	SDS	8.5
38	10.0	SDS	3.0
39^d	0.5	CTAB	32.6
40	0.5	CTAB	34.7
41	0.75	CTAB	54.9
42	1.25	CTAB	76.5
43	1.25	CTAB	84.3
44	1.50	CTAB	78.2
45^d	10.0	CTAB	15.3

^{a}Abbreviations as in Tables 2 and 4.
^{b}[(mol/L) × 10^3].
^{c}Experiment from matrix C (Table 4).
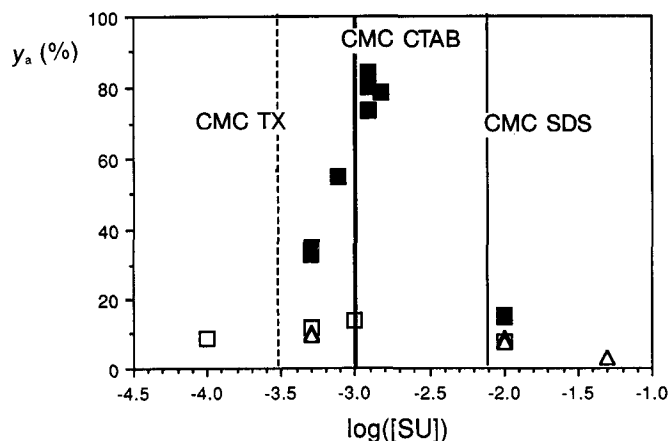^{d}Experiment from matrix A (Table 2).

FIG. 3. Variation of the affinity (y_a) as a function of the surfactant concentration: ■, CTAB; △, SDS; □, TX (F, cotton; [F], max). Abbreviations as in Tables 2 and 4.

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