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RESEARCH PAPER

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Optimization with Experimental Design of Nonionic, Anionic, and Amphoteric Surfactants in a Mixed System

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ABSTRACT

In a mixture experiment the response depends only on the relative proportions of material present in the mixture. In this study, we consider shampoo formulations with three different classes of surface-active agents: amphoteric, nonionic, and anionic mild surfactants. A major purpose of this study is to help the formulator with a strategy using a three-component simplex-centroid design. This methodology offers the maximum return in terms of information about the interplay of multiple factors while requiring the minimum investment.
***Key Words**: Experimental design, Formulation, Optimization, Shampoo, Surfactant*

INTRODUCTION

All formulations are by definition mixtures, and to investigate the effects of different proportions of components we must use experimental designs (1). This method needs only a limited amount of experimentation. Let a mixture system consist of *n* ingredients, and in mixture experiments the choice of a design must be based on the particular model to be fitted. Typically, mixture models proposed in the literature are simplex lattice, simplex centroid, or axial design (2–4).

After the appropriate model was chosen, its adequacy was tested. Then a graphical response surface was represented. To illustrate how this experimental methodology can be applied, we have described a mixture of surfactants used in the field of hair care. In this study, the formulation is a liquid system consisting of water that is combined with minor components and three active

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ingredients: nonionic (Oramix CG 110®), anionic (Texapon SB3®), and amphoteric (Dehyton K®) surfactant. The major shampoo functions are to emulsify oils and remove dirt and debris from the hair and scalp. The nonionic shampoos are generally poor foaming agents, but they are compatible with a wide variety of systems. The anionics such as sufosuccinates have a low irritation potential and afford improved rinsability. The outstanding feature of amphoteric components is low eye and skin irritation. The amphoteric components are also considered as moderate-to-good detergents.

The possible functions in each product category are chosen by the formulator. Each surfactant used should be included for a specific reason and to accomplish a function: detergency, foam, skin compatibility, and low level of irritation. When the surfactant selection was established, an unlimited percentage of all raw material could be tested. Our strategy was to investigate an appropriate experimental design.

The principal and ideal properties of a shampoo are: it should be viscous enough to stay in the hand before application, and the lather must be dense and luxurious but without a high surfactant concentration. This lather must be stable and persistent with oil, and should rinse out easily. Usually a concentration of 12–20% of surfactant is required to develop an acceptable lather (5). We have chosen a concentration of 18%.

MATERIALS AND METHODS

Raw Materials

A nonionic caprylyl/capryl glucoside (Oramix CG 110, SEPPIC), an anionic disodium laureth sulfosuccinate (Texapon SB3, Henkel), and an amphoteric cocamidopropyl betaine (Dehyton K, Henkel) surfactant were used. Cocamide DEA (Oramix DL 200®, SEPPIC) and sodium carboxymethyl cellulose (Blanose®, Hercules) acted to regulate and stabilize the viscosity grade. A preservative (Kathon CG®, Rhom and Haas), fragrance, and color were considered as additives. Distilled water was used for all formulations. Artificial soil ingredients were paraffine liquid (Primol 352®, ESSO), lanolin (Prolabo), and dioxan (Merk).

Instruments

To produce the shampoo formulation, a homogenizer (Turbotest 33/300, Rayneri) was used. The viscosity of shampoos was studied with a Rheometer (Rheomat 108, Contraves).

Preparation of Shampoo

Ingredients and their concentrations are listed in Table 1. "A" ingredients were heated (60°C) and homogenized at 400 rpm for 5 min, then "B" ingredients were added at room temperature. Two hundred grams of shampoo was prepared for each studied point.

Experimental Design Construction

In a q-component simplex-centroid design, the number of points is $2^q - 1$. At the point of the simplex-centroid design, data on the response were collected and a polynomial was fit that had the same parameter to be estimated as there were points in the associated design (6). The 7-point design is shown in Fig. 1. To check on the adequacy of the fitted model, three additional points were prepared and are shown in Fig. 2.

The quadratic model is described in the following equations:

$$Y = \beta_1 X_1 + \beta_2 X_2\ \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

Table 1

Composition of Shampoo Formulation

	Ingredients	% (w/w) Active Ingredients
"A"	Σ (Dehyton K / Oramix CG 110 / Texapon SB3)	18
	Oramix DL 200	2
	Blanose	2
	Distilled water	qs 100
"B"	Kathon CG	0.0015
	Fragrance and color	0.3

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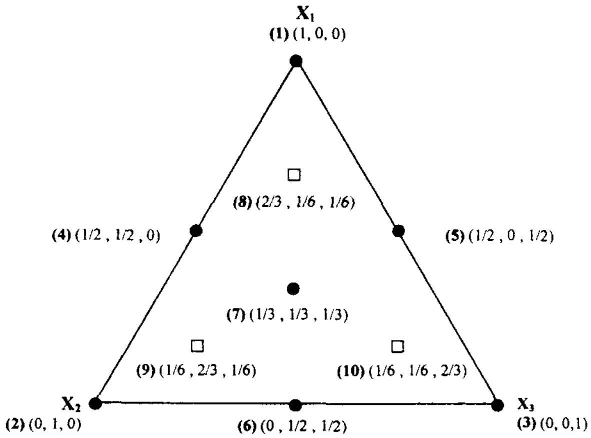

Figure 1. Three components, 7-point designs (●), and 3 check points (□). Simplex centroid design.

$$0 \leq X_i \leq 1 \text{ for } i = 1, \ldots q$$

$$\sum_{i=1}^{q} X_i = 1$$

where $q = 3$ components.

Studied Factors

Three factors were analyzed: Texapon SB3 (X_1), Dehyton K (X_x), and Oramix CG 110 (X_3). To simplify the establishment of the phase diagrams, we considered in each vertex of ternary diagram an aqueous solution

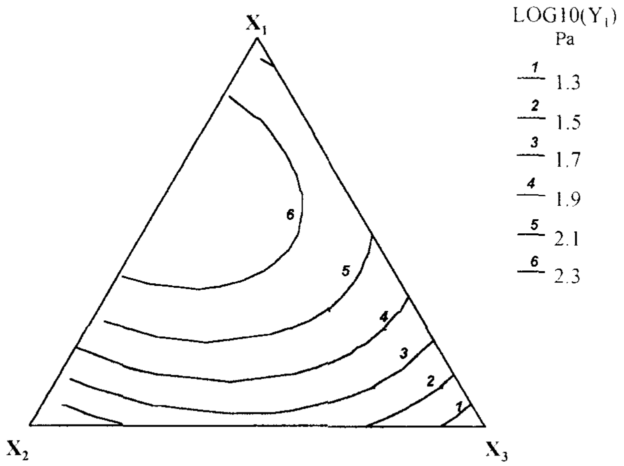

Figure 2. Contours of estimated response surface [corresponding to the fitted model represented by Eq. (2)].

of the diverse components, with the surfactant concentration limited to 18% (w/w).

Studied Responses and Measurement

Three responses were studied. The first corresponds to the viscosity evaluation (Y_1), the second to the foam stability with soil (Y_2), and the last response determines the wetting power (Y_3).

The flow behavior was obtained for each formulation. Shear stress is a function of rate, $\log(\tau) = f[\log(D)]$, where τ is shear stress and D is share rate, were measured respectively in Pascals (Pa) and in seconds $^{-1}$ (sec^{-1}). These formulations had a pseudoplastic flow behavior, and to compare them we chose the $\log(\tau)$ at $D = 1290\ sec^{-1}$. All surfactant mixtures obtained were good foaming agents, and when the Ross-Miles method (7) is used, at 25 ± 1°C after 5 min, a 13.42-cm foam height (with a standard error $s = 0.49$) with a 5-g·liters^{-1} shampoo dilution resulted. The quality of the lather can drop drastically in presence of oily soils (oily substances, sebum, lipids, cell debris, etc.). To measure the soil interaction on the foam, an artificial soil was prepared with 2.5% (w/w) lanolin and 2.5% (w/w) paraffin liquid in dioxan (8). On the foam obtained with Colson methodology, 1 ml of artificial soil was added and the resulting height was measured (9). This height corresponded to the second response (Y_2). Wetting is the displacement from a surface of one fluid by another. A wetting agent is a substance that promotes this effect. Good wetting characteristics enable the detergent to come into intimate contact with the surface to be cleaned (10). The last response (Y_3) is the wetting power, which is given by the surfactant concentration, (g·liters^{-1}) where a cotton tissue disk (2 cm diameter) was completely immersed in the liquid, with a wetting time of 100 sec (11).

RESULTS AND DISCUSSION

Matrix Notation

The matrix notation, the experimental data of the three responses, and the estimated data are reported in Table 2. The following data were collected at the points 1–7 of the simplex-centroid design. The points 8–10 were chosen and observations were collected to check the fit on the quadratic model. All experiments were performed in random order and calculations were obtained by the Statgraphics program (12). The calculations give were

Table 2

Matrix of Simplex-Centroid Design and Responses

Points	Factors X_1 Texapon	X_2 Dehyton	X_3 Oramix	Observed Responses Y_1 log(τ) Pa	Y_2 Foam Height, cm.	Y_3 Wetting Power, g·liters²	Estimated Responses Y_1'	Y_2'	Y_3'
Design points									
1	1	0	0	2.041	5.5	3.0	2.026	5.5	3.0
2	0	1	0	1.246	2.5	2.9	1.230	2.5	2.9
3	0	0	1	1.149	4.5	6.0	1.134	4.5	6.0
4	0.5	0.5	0	2.361	3.0	3.2	2.422	2.8	3.1
5	0.5	0	0.5	2.041	3.0	4.2	2.102	2.8	4.1
6	0	0.5	0.5	1.561	1.0	3.9	1.621	0.8	3.8
7	0.333	0.333	0.333	2.380	1.0	3.3	2.244	1.4	3.5
Check points									
8	0.667	0.167	0.167	1.740	2.50	4.00	2.378	3.0	3.3
9	0.167	0.667	0.167	2.699	1.50	3.40	1.952	1.3	3.2
10	0.167	0.167	0.667	1.520	2.00	4.40	1.814	2.0	4.5

$$log(Y_1) = 2.026X_1 + 1.230X_2 + 1.134X_3 + 3.176X_1X_2 + 2.087X_1X_3 + 1.758X_2X_3 \quad (2)$$

$$R^2 = 0.98$$
$$R_A^2 = 0.88$$

$$Y_2 = 5.549X_1 + 2.549X_2 + 4.549X_3 - 4.984X_1X_2 - 8.984X_1X_3 - 10.984X_2X_3 \quad (3)$$

$$R^2 = 0.98$$
$$R_A^2 = 0.89$$

$$Y_3 = 3.027X_1 + 2.927X_2 + 6.0X_3 + 0.799X_1X_2 - 0.583X_1X_3 - 3.411X_2X_3 \quad (4)$$

$$R^2 = 0.99$$
$$R_A^2 = 0.92$$

Design Evaluation

There are several approaches to the examination of the quality of experimental designs. First, the value of R^2, which is the square of the multiple correlation coefficient; R^2 is in each case ≥0.98. Some analysts prefer to select the model that maximizes the adjusted R^2 represented by R_A^2; these values are in all cases greater than or near 0.90. But the R^2 statistic is not the only criteria used in determining how well the model fits the data. In addition to R^2 values, the simplest way to judge the goodness of a fitted model is to examine the estimation of the model parameters and compare them with data at predefined points. In our case, for these extra points, called "check points," we have compared the observed response values with calculated responses. If the difference between predictions and experimental data is smaller than the confidence limit of the method, the model is fitted. This approach is required for unreplicate observations (13).

We shall consider the fitting of the quadratic model in Eqs. (2,3,4) to data values collected at the point of the simplex-centroid design.

The standard error of each method was determined by carrying out replicate measurements in order to measure the repeatability of the proposed procedure. In our case, the $2s$ confidence limit is then calculated as $Y \pm t$ $(ddl, \alpha) \times s$ (with appropriate t values at $\alpha = 5\%$ (14). For each studied response we have, respectively, $Y_1 \pm 0.52$, $Y_2 \pm 0.74$, and $Y_3 \pm 0.75$.

In all cases, experimental data are in good agreement with the calculated values, since discrepancies are comparable to the experimental error.

Graphical Procedure for Mixture

A response surface is the graph of a system response plotted as a function of the system factor (15). Therefore, the model is suitable to the description of the stud-

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ied variables, and Figs. 2, 3, and 4 illustrate the contour diagrams obtained from Eqs. (2,3,4), respectively. The mixture of these three different surfactants increases the amount of log(τ) with a synergistic action. To obtain a satisfactory viscosity, we must use a composition in the shaded region (Fig. 2). Conversely, the mixture conduces to a drastic deterioration of foam height. These blends give an antagonistic action and the shaded region corresponds to compatible compositions for shampoo formulations (Fig. 3). The wetting power is affected by increasing amphoteric and anionic concentrations; the shaded area in Fig. 4 indicates all compositions that have an acceptable wetting power (>4.1 g·liter^{-1}). In the last step, individual contour plots of the different responses were superimposed and give an optimum zone (Fig. 5). The combination of nonionic and anionic products with the lowest concentration of amphoteric products forms an acceptable shampoo.

CONCLUSION

Generally, screening designs are recommended for any mixture problems and provide much information. The fitted model in the mixture components can be used to predict values of responses at any point inside or on the boundary of the triangle. The graphical procedure is an important tool for understanding the region of interest. Several interesting conclusions have surfaced in this paper. First, this amphoteric surfactant has an antagonistic effect on our optimum conditions. Second, the nonionic surfactant has a good action on all responses tested. Finally, the region of interest is very limited. This screening design provides much information and allows the researcher to make decisions based on results for all concentrations of surfactants.

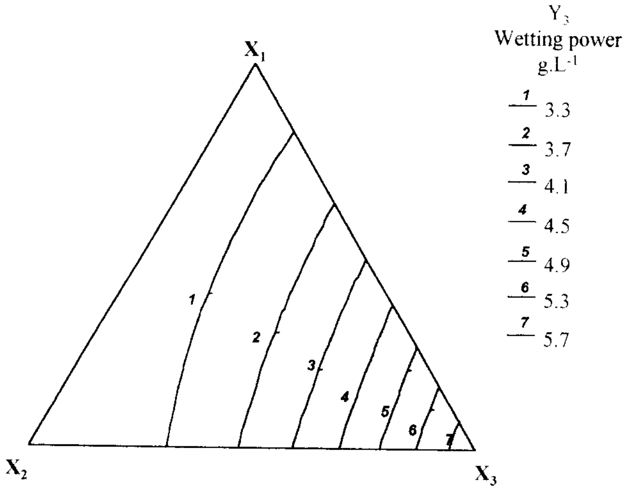

Figure 4. Contours of estimated response surface [corresponding to the fitted model represented by Eq. (4)].

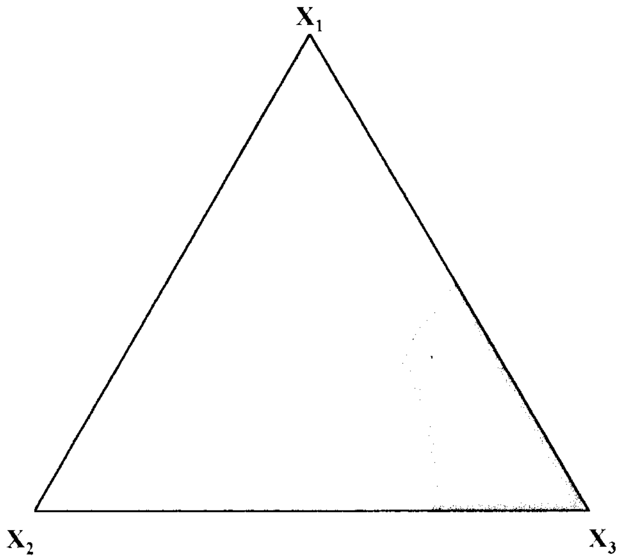

Figure 5. Region of interest obtained by superimposing Figs. 2,3, and 4.

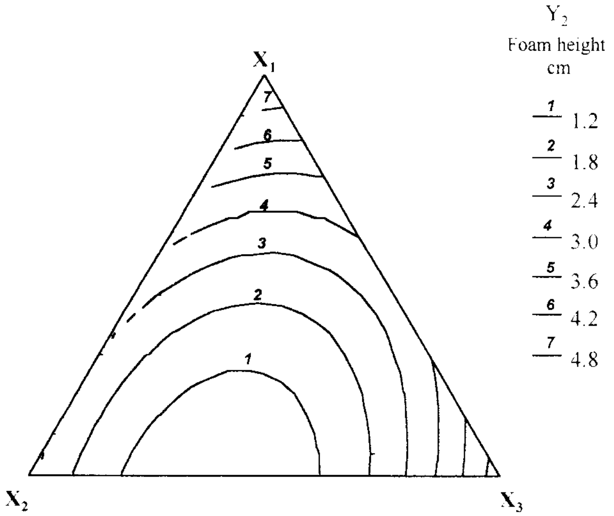

Figure 3. Contours of estimated response surface [corresponding to the fitted model represented by Eq. (3)].

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