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ORIGINAL PAPER

Prediction of the surface tension of surfactant mixtures for detergent formulation using Design Expert software

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Abstract The formulation of a detergent product is a complicated task which depends on many economical, ecological, and practical parameters. The goal is to achieve a product which will have optimal washing properties and significantly decrease the surface tension. Therefore, prediction of the minimal surface tension of a mixture of four different surfactants can be very beneficial for the industry. In this work this task was performed by using Stat-Ease Design Expert software. This program was successfully applied for prediction of the minimal surface tension and optimization of the composition of different surfactant mixtures. Predicted data were compared with experimental results, and very good correlation was achieved. For further application, more complex optimization procedures could be performed by adding additional parameters to the Design Expert software. Therefore, this program is extremely useful for the laundry industry and could be successfully applied in many other, more complex tasks.

Keywords Surface tension · Optimization · Surfactants · Design Expert

Introduction

The formulation of a detergent or soap product is a complicated task. Many compounds need to be combined and dosed carefully. These components originate from six main groups: bleaching agents, builders, enzymes, fillers, surfactants, and other additives such as dispersing agents, dye-transfer inhibiting ingredients, fabric softening clay, and optical brighteners [1]. It is known that surfactants are the most important ingredients in cleaning products, since they significantly change the surface tension of water, playing a leading role in washing processes [1, 2]. At the same time, many commonly used surfactants are highly toxic. This is the reason why many studies concerning their biodegradability have been performed [3–14]. Therefore, their formulation and development should be based on economical and environmental considerations.

During the creation of a new detergent product, the ability to predict the behavior of complex mixtures can be very useful. Optimization of a detergent composition can be performed by different methods such as nonlinear mapping [15], partial least-squares analysis [16], principle component analysis [17], genetic algorithms [18, 19], and artificial neural networks [20, 21]. Some of those models have already been tested for different optimization procedures and for prediction of mixture behavior [22–24]. For scientific or industrial purposes, software programs such as Design Expert might be more useful in optimization of complex systems [23]. Nevertheless, to the best of the author's knowledge, this program has not been applied for any detergent formulation until now.

Optimization is the process of finding the best available values of some objective function in a defined domain. In this work, the optimization goal is to find the composition of a mixture of four surfactants which will have the minimal surface tension. Before the optimization, preliminary experiments were created based on design of experiments using the response surface methodology [25]. The response surface methodology allows performance of calculations at levels that were not previously studied experimentally, as well as the performance of predictions [26]. The advantage of such an approach is that, while applying the

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experimental design, large numbers of optimization experiments are not needed. The experimental design was based on the aim of determining the sensitivity of the system to each studied surfactant. According to the literature, the behavior of the system can be verified in the dependence on the incorporated factors [27].

The software program used was Stat-Ease Design Expert (DX6), which is able to apply different designs: randomized block and lattice designs, crossover designs, split plots, nesting, repeated measures, and covariates [28]. Due to the fact that a large quantity of information can be produced in a very short time for various conditions of interest, visualization of results is very important. This program offers the facility of examining the results for each solution one at a time graphically. At the end of the optimization and prediction process, a decision is taken regarding which design to use and how many levels to set for the known factors [29].

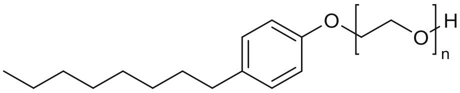
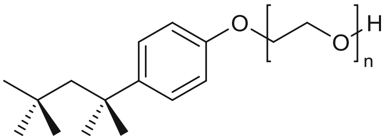
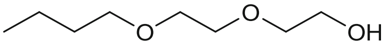
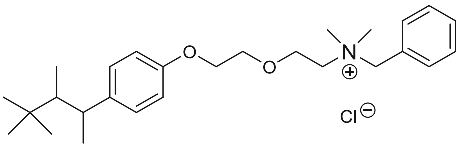
For this reason, to perform complex optimization experiments, it was necessary to specify the order of the polynomial. It is known that first-order polynomials model linear behavior, those of second order reveal two-component interactions, while more complex interactions can be modeled only by third-order polynomials. Such modeling is a very complex task, but the DX6 software is able to handle multiparameter optimization tasks easily. For proper optimization it was important to generate a good candidate set. The selection procedure involved matrix calculation designed to produce precise model coefficients [30].

The procedure for finding the optimal formulation for mixtures using DX6 is not described herein, since it was described in detail by Anderson and Whitcomb [31]. Those authors presented a relatively simple study on finding the optimal formulation of three surfactants. With large numbers of factors, only a fraction of the runs needed to be completed to produce estimates of main effects and simple interactions [31]. Similar optimization investigations were reported recently, showing that this approach will find broader application in the near future [31–36]. The main objective of this work is to use Design Expert 6 software for prediction and composition optimization of a mixture of four surfactants with the minimal surface tension. The goal was to test whether such software can be useful for the laundry industry.

Results and discussion

The main goal in detergent formulation is the achievement of an efficient cleaning product, and the main purpose of surfactants in the detergent formulation is to reduce the surface tension. The purpose of this investigation is to predict the minimal surface tension of different surfactant mixtures. The surfactants investigated are described in Table 1.

Table 1 Surfactants investigated

Trade name	IUPAC name	Property	Structure
NF-9	Alkylphenol polyglykolether	Nonionic	
Tritone X-100	*t*-Octylphenoxy-polyethoxyethanol	Nonionic	
Lyogen BPN	Diethyleneglycol monobutylether	Nonionic	
Hyamine	Benzethanium chloride	Cationic	

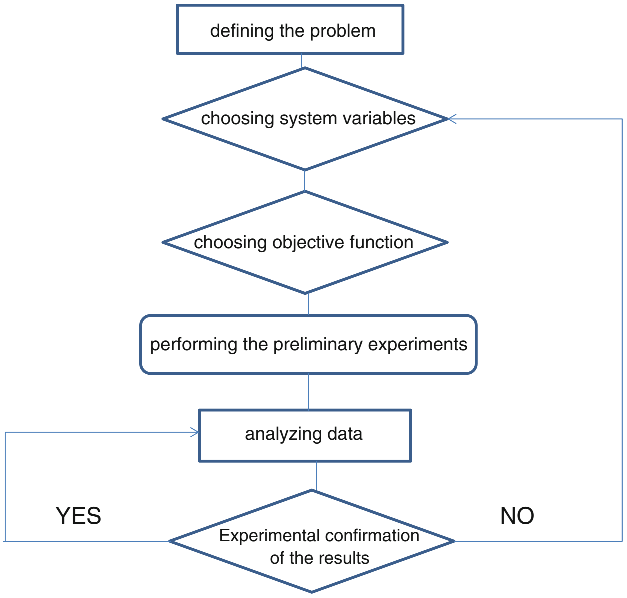


Fig. 1 Algorithm of the experimental design applied for prediction of minimal surface tension

Design of experiments

In this method, the classical approach of changing one variable at a time is replaced by the possibility of simultaneously optimizing a multivariable system using experimental design. This approach has many advantages, including the performance of a minimal number of experiments and simultaneous determination of input level of responses. It was important to organize the experiment in such a way that correct data could be collected and computed. Therefore, the applied response surface methodology connects the output variable (the resulting surface tension) to all of the input variables that affect it (the volume ratios of the four different surfactants) together. The general algorithm of the experimental design is shown in Fig. 1.

The detailed steps of the algorithm used and presented in Fig. 1 are: (1) define the problem as finding the optimal composition of a mixture of the four surfactants with the minimal surface tension; (2) choose the system variables and ranges of variation for each, i.e., the volume ratios of surfactants for testing in preliminary experiments, with temperature, pressure, and all other parameters kept constant; (3) choose the objective function and experimental design methods, incorporating the most appropriate experimental design into the Design Expert program package with the goal of achieving minimal surface tension, while keeping all other parameters within the domain of the input data; (4) perform the preliminary experiments (60 different combinations of surfactants) and obtain the responses (measuring the weight of the solution, monitoring the temperature and the pressure); (5) analyze the data (calculation of the average surface tension from triplicate experiments, incorporating this into the Design Expert software) and reach conclusions about the system (listing the recommended optimal mixtures); (6) decide on the desired optimal surfactant mixture composition; and (7) carry out experimental confirmation of the proposed calculated optimal mixtures of surfactants and comparison with experimental data. Final conclusions were then reached based on the responses for each surfactant investigated.

It is often necessary to investigate several different effects on a response of interest: the total factorial experiment consists of an equal number of replicates for all possible combinations of all the factors investigated. It can be shown that there are many reasons for designing a complete factorial experiment rather than performing one investigation for each particular factor individually. Firstly, factorial experiments are more efficient for estimation of main averaged effects. Secondly, interactions between different factors can only be assessed in the specific factorial experiment. Therefore, the classical approach of changing one variable at a time should be replaced by optimization of multivariable systems using experimental design.

In this work, this approach has many advantages, including the need for the minimal number of experiments to be performed, and the possibility of simultaneous determination of input level of responses. The experimental design was based on statistical analysis which aimed to determine the sensitivity of the system to each of the parameters studied. In this work, the behavior of the system was verified depending on the incorporated factors, as was recommended in the literature [27]. The DX6 software allows application of different designs: randomized block and lattice designs, crossover designs, split plots, nesting, repeated measures and covariates. The results of each optimized solution were examined one at a time, after which the decision about which design to use was taken. The response surface methodology connects the output variable (surface tension) to the input variables (the volume ratios of each surfactant), allowing calculations to be performed at intermediate levels not studied experimentally, as well as performance of predictions for systems that were not experimentally checked in the first step. For this reason, there was no need for a large number of optimization experiments. Therefore, in this experiment it was first necessary to specify the order of the polynomial. First-order polynomials model linear behavior, second-order polynomials reveal two-component interactions, while more complex interactions can be modeled by third-order polynomials. After this step, it was important to generate a candidate set: for mixtures, usually a third-order mixture model called a "special cubic" is chosen. The selection procedure involved matrix calculation designed to produce precise model coefficients.

Table 2 Data collected from preliminary tests: surface tensions (γ/N m^{-1}) of mixtures of Tritone X-100 (TRIT), NF-9, Hyamine (HYA), and Lyogen (LYOG) surfactants

TRIT	NF-9	HYA	LYOG	γ/N m^{-1}	TRIT	NF-9	HYA	LYOG	γ/N m^{-1}
100	0	0	0	37.8770	40	0	40	20	40.4548
80	20	0	0	36.7801	20	20	40	20	41.1832
60	40	0	0	36.9470	0	40	40	20	41.1606
40	60	0	0	37.0443	20	0	60	20	43.1161
20	80	0	0	38.6522	0	20	60	20	43.6098
0	100	0	0	38.7652	0	0	80	20	52.1065
80	0	20	0	37.8526	60	0	0	40	37.4355
60	20	20	0	38.2368	40	20	0	40	37.3868
40	40	20	0	38.6279	20	40	0	40	37.2616
20	60	20	0	38.9147	0	60	0	40	37.3746
0	80	20	0	39.3562	40	0	20	40	40.5052
60	0	40	0	44.1156	20	20	20	40	42.8085
40	20	40	0	40.3557	0	40	20	40	42.7876
20	40	40	0	40.7104	20	0	40	40	45.5914
0	60	40	0	41.1693	0	20	40	40	45.3255
40	0	60	0	41.5308	0	0	60	40	56.6694
20	20	60	0	42.1531	40	0	0	60	43.9435
0	40	60	0	42.2644	20	20	0	60	43.0692
20	0	80	0	43.1891	0	40	0	60	43.1040
0	20	80	0	44.0896	20	0	20	60	45.4767
0	0	100	0	58.6615	0	20	20	60	45.7166
80	0	0	20	37.0843	0	0	40	60	53.0764
60	20	0	20	37.0982	20	0	0	80	46.1963
40	40	0	20	37.2442	0	20	0	80	47.2080
20	60	0	20	37.2877	0	0	20	80	50.1301
0	80	0	20	37.3068	0	0	0	100	50.1839
60	0	20	20	39.6431	50	50	0	0	35.7458
40	20	20	20	39.7352	45	55	0	0	35.8988
20	40	20	20	38.9982	70	30	0	0	35.8241
0	60	20	20	39.0329	75	25	0	0	35.0923

Response surface methodology using Box–Behnken design was used to optimize the response of the four input variables (the volume ratios of the four surfactants in the mixture) and one output variable (the surface tension of the resulting mixture) [28]. For the purpose of this investigation, collection of preliminary experimental data included performance of 60 individual experiments with different combinations of volume ratios of the surfactants. Thus, in preliminary tests, the volume ratios of investigated surfactants were changed from 0 to 100% in steps of 20%, and the obtained results are presented in Table 2.

It has to be emphasized that, on increasing the number of components in the mixture, the number of preliminary experiments needed for the optimization also increases. While only 11 mixtures would be sufficient to optimize a binary mixture, 60 mixtures of four surfactants were prepared as the minimal possible testing set for this mixture optimization.

The optimization process involved studying the responses of the statistically designed combinations, estimating the coefficients by fitting them using the mathematical model that best fitted the experimental conditions, predicting the response of the best-fit model, and checking the adequacy of the model. For all calculations the Stat-Ease Design Expert computer program was used. Other methods such as genetic algorithms or artificial neural networks could also be performed for such a complicated optimization task, but they would also demand prior modeling of the experimental data. The modeling step is the largest source of error in cases where there are insufficient data to describe the whole experimental regime. In this respect, the 60 preliminary tests used for DX6 would not be sufficient.

The results (the distribution of surface tension as a function of the four investigated surfactants) of the preliminary experiments are shown in Fig. 2.

To enable ternary display of the results, the volume of Lyogen was kept constant at 25%. It is not shown, since it can be expressed as D = 100% − A – B − C.

After collecting the experimental results, the data were processed. The result was the prediction of the optimal mixture of the investigated four surfactants (Tritone-X, NF-9, Hyamine, and Lyogen) which will have the minimal surface tension. The optimization process included deciding on the mathematical parameters to be used and their effects on the calculation. The DX6 program offers the possibility to check the results using various graphical displays, as presented in Figs. 3 and 4.

Figure 3 shows the standard error of the design applied, while Fig. 4 presents the normal plot of residuals. Such graphics are extremely useful for optimization of complex systems such as multivariable optimization. The results of the prediction of minimal surface tension are given in Table 3.

As can be seen from Table 3, using the DX6 program many slightly different optimal solutions can be predicted. In addition, several different points with maximal surface tension can be chosen, although this was not done in this experiment. Each user should decide which of the offered candidate solutions would be the most useful and favorable. For the laundry industry, many important ecological and economical parameters could be considered in this step of the optimization; for instance, the least harmful or expensive surfactants would have priority.

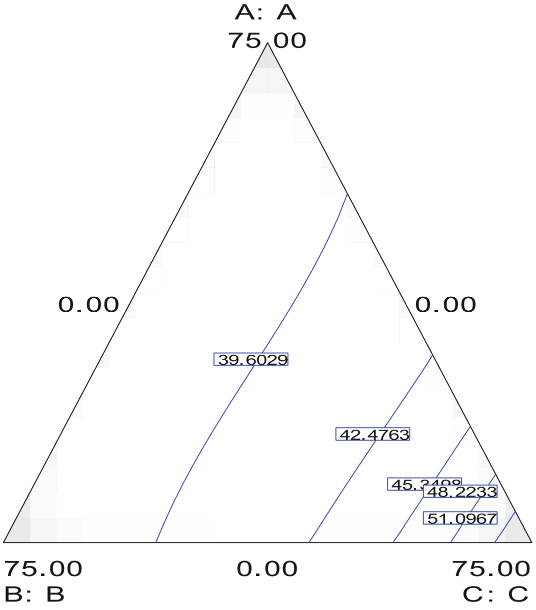


Fig. 2 Distribution of the surface tension as a function of the four components (A = Tritone, B = NF-9, C = Hyamine, D = Lyogen = 25%)

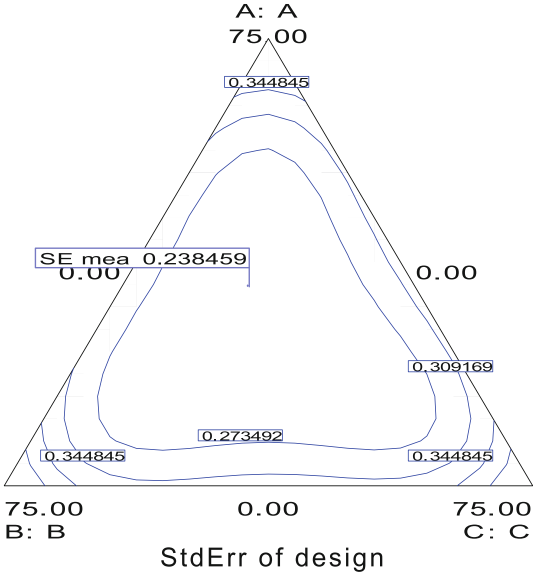


Fig. 3 Graphical display of the standard error of the design

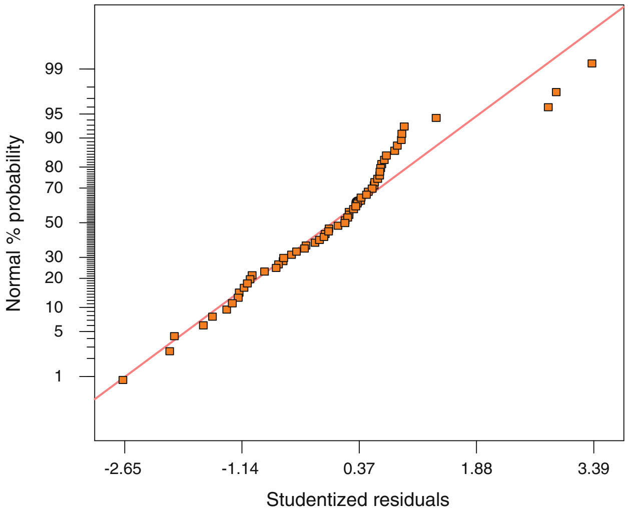


Fig. 4 Normal plot of residuals

After choosing the most appropriate predicted candidate solutions, experiments covering the desired mixtures were performed, and the predicted and experimental data were compared. The results of the comparison are also presented in Table 3. As can be seen from Table 3, very good correlation between experimental and predicted data was achieved, with relative errors below 10%, and for the majority of the mixtures less than 2%. Therefore, it can be

Table 3 Results of the prediction (PRED) of minimal surface tension (γ/N m^{-1}) for Tritone X-100 (TRITONE), NF-9, Hyamine (HYAM), and Lyogen (LYOG) mixtures compared with experimental data (EXP), with errors and coefficient of variation (CV)

TRITONE	NF-9	HYAM	LYOG	EXP	PRED	Error	CV/%
69	24	0	7	34.7116	35.6669	−0.9553	−2.75
70.5	22.5	0	7	33.2549	35.6780	−2.4231	−7.29
79	10	0	11	35.6862	35.9894	−0.3032	−0.85
43	44	0	13	36.0900	36.0675	0.0225	0.06

concluded that the optimization procedure is valid. The result of the optimization (Fig. 5) is the minimal surface tension of 33.2549 N m^{-1} for the mixture of 70.5% Tritone-X, 22.5% NF-9, 0.0% Hyamine, and 7.0% Lyogen.

In conclusion, the results obtained demonstrate the possibility of applying Stat-Ease Design Expert software for prediction and optimization of surface tension while formulating complex mixtures of surfactants. The optimization goal was minimization of the surface tension by calculating the optimal ratio of surfactants in the mixture. Optimization using Design Expert software was a very appropriate choice for this complex task, due to the need for only a small number of preliminary experiments, and no requirement for a real model of the experimental data. Due to its simple usage and the wide range of possibilities offered to different users, Design Expert software will probably find application in many different industries (such as the laundry industry) in the near future.

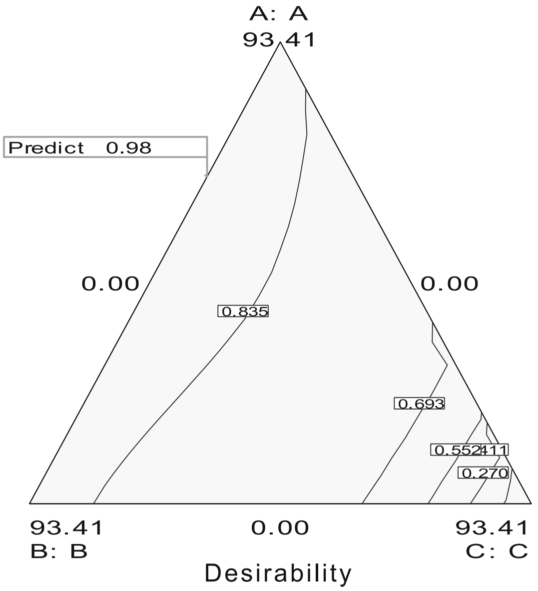


Fig. 5 Result of the optimization, showing the desirability of optimal volume ratios among the four surfactants investigated

Experimental

Reagents and samples

Standard solutions (1 g dm^{-3}) of surfactants were prepared by dissolving accurate quantities of powdered and liquid reagents in water. The investigated surfactants Tritone X 100, NF-9, Hyamine, and Lyogen were of highest purity, supplied by Merck (Germany).

Determination of surface tension

Surface tension was determined by a stalagmometer using water as the reference material [37]. In this device, when hanging drops start to fall, their volume reaches its maximum value, and the weight of the drop comes into equilibrium with the surface tension. Therefore, according to Tate's law, $mg = 2\pi r\sigma$. In other words, the drop falls at the precise moment when the weight (mg) becomes equal to the circumference ($2\pi r$) multiplied by the surface tension (σ). Using this equation, the surface tension was calculated using the known radius of the tube (r) and the mass of the fluid droplet (m). Secondly, using a reference fluid (for example, water), the surface tension of the investigated solution of tenside could be calculated from the ratio $m_1/\sigma_1 = m_2/\sigma_2$, where m_1 and σ_1 are the mass and surface tension of the reference fluid (for example, 20 drops of water), and m_2 and σ_2 are the mass and surface tension of the surfactant solution (for example, 20 drops of nonionic or cationic surfactant). In this work, experiments were performed in triplicate at constant temperature and pressure, and calculations were based on the expression

$$\sigma = \sigma_{\mathrm{H_2O}} \times \frac{m}{m_{\mathrm{H_2O}}}, \tag{1}$$

where σ is the surface tension of the investigated mixture of surfactants expressed in N m^{-1}, σ_{H2O} is the surface tension of water in N m^{-1}, m_{H2O} is the mass of the reference water expressed in g, and m is the mass of the investigated surfactant mixture in g.

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