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MATHEMATICAL MODEL OF SULPHOMETHYLATION PROCESS OF NONYLPHENOL

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Abstract: This paper concerns the development of the mathematical model of sulphomethylation process of nonylphenol based on planning of the experiment. While developing the mathematical model of the process, a method of gross factor experiment (GFE), realizing all possible combinations of the factors chosen, was used by us. By varying four factors on two (minimum and maximum) levels, the experimental values of yields of the product required (sodium sulphate of hydroxynonylbenzyl sulphonic acid), were obtained. The coefficients of regression equations B_i are calculated by scalar products. Then the adequacy of the mathematical model was checked. Thus, a mathematical model of the sulphomethylation process of nonylphenol in the full scale of coordinates was obtained.

1. INTRODUCTION

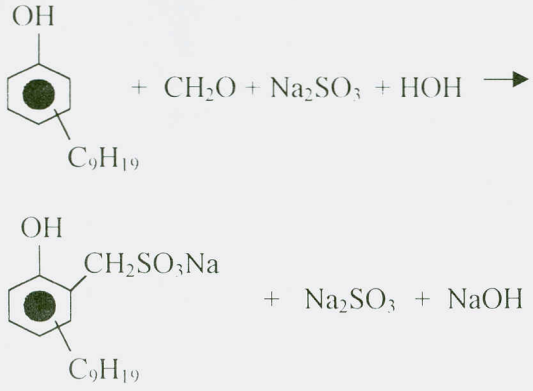
It is known that sulphonate additives based on sulphonated alkylphenols possess detergent-diapersive, antioxidative and anticorrosion properties. Initial alkylphenol is sulphonated mainly by oleum, concentrated sulphuric acid and sulphuric anhydride. By saponification of alkylphenol sulphonic acids through oxides or hydroxides of alkaline-earth metals, efficient sulphonates are obtained.

The main shortcoming of these methods for obtaining the sulphonate additives considered is the application of aggressive reagents (oleum, concentrated sulphuric acid and sulphuric anhydride) as sulphonating agents which lead to environmental contamination. In addition, the sulphonation process promotes the formation of considerable amount (35-40%) of acid sludge requiring further utilization. Furthermore, the gelatinous sludge, generated on neutralization step, does not dissolve in organic solvents.

To protect the purity of the ambient environment and to eliminate these drawbacks, a new method of manufacturing the multifunctional additives to lubricating oils, based on sulphomethylated alkylphenols (hydroxyalkylbenzyl sulphonic acids), has been developed at the Institute of Chemistry of Additives, Azerbaijan Academy of Sciences [1-3].

2. MATHEMATICAL MODELLING

The sulphonation process of alkylphenol or nonylphenol may schematically be represented as follows:



(1)

The sodium salt of hydroxynonylbenzyl sulphonic acid (HNBSA) obtained is a starting material for the production of multifunctional additives to lubricants.

In developing the mathematical model, the following factors, affecting the process, have been chosen:

Z_1 – the amount of Na_2SO_3, (g);
Z_2 – the amount of formalin, (mL);
Z_3 – the amount of heptane, (mL);
Z_4 – the amount of nonylphenol, (g).

The minimum and maximum levels of the factors considered were:

$$\begin{array}{ll} 40 <= Z_1 <= 70 & 90 <= Z_3 <= 110 \\ 30 <= Z_2 <= 60 & 40 <= Z_4 <= 70 \end{array} \qquad (2)$$

While developing the mathematical model of the process, a method of gross factor experiment (GFE), realizing all possible combinations of the factors chosen, was used. A number of experiments needed N at GFE is determined by the formula as below:

$$N = L^k \qquad (3)$$

where L – a number of levels; k – a number of factors.

Considering that L = 2 and k = 4, a number of experiments needed is

$$N = 2^4 = 16$$

By varying four factors on two (minimum and maximum) levels, the experimental values of yields of the product required (sodium sulphate of hydroxynonylbenzyl sulphonic acid), were obtained (Table 1).

The coefficients of regression equation B_i are calculated by scalar product of Y^{ex} column on appropriate column X_j, divided by a number of experiments in the matrix of planning N:

$$B_j = 1/N\left(\sum_{i=1}^{N} X_{ji} Y_i^{ex}\right) \quad (4)$$

Thus, a following mathematical model of the process in dimensionless co-ordinate system was obtained by us:

$$Y_N = 105.875 - 0.375X_1 + 3X_2 + 7.8125X_3 + 1.1875X_4 + 0.75X_1X_2 + 2.5625X_1X_3 + \\ +0.1875X_1X_4 + 1.8125X_2X_3 + 0.6875X_2X_4 - 3.125X_3X_4 \quad (5)$$

To check the adequacy of the mathematical model obtained, a residual dispersion was calculated by formula as follows:

$$S^2_{rem} = M\sum_{N=1}^{16}\left(\overline{Y}_N - Y_i^{ex}\right)^2 / F \quad (6)$$

where $F = N - k - 1$ is a number of degrees of freedom; N - a number of experiments; M – a number of parallel experiments; k - a number of factors (in the given case $N = 16$; $M = 3$; $k = 4$).

For each group of parallel experiments, the selected dispersions were estimated according to formula:

$$S^2_N = \sum_{k=1}^{M}\left(Y_{Nk} - \overline{Y}_N\right)^2 /(M-1) \quad (7)$$

where Y_{Nk} – experimental values of the output parameter; Y_N – an average value of the output parameter obtained from the results of parallel experiments and calculated by formula:

$$\overline{Y} = \sum_{k=1}^{M} Y_{Nk} / M \quad (8)$$

Experimental errors were determined by the formula:

$$S_0 = \sum_{N=1}^{M}\sum_{k=1}^{M}\left(Y_{Nk} - \overline{Y}_N\right)^2 / N(M-1) \quad (9)$$

In the development of the mathematical model, its adequacy was checked by minimizing the differences of squariances of experimental (Y^{ex}) and estimated (Y_N^{est}) values. It is considered that the mathematical model adequately describes this particular process in the case of residual dispersion S^2_{res} of the output value Y^{ex}_N, estimated by formula (6) relative to the average experimental values Y_N, atatistically does not exceed the errors of the experiment S^2_0.

Tabulated values of Fisher criterion for P=0.05 is f_1=N-k-1 = 11; f_2=M-1 = 2.

Therefore

$$F_{1-p}(f_1,f_2) = 19.41$$

Fisher criterion was calculated from the formula:

$$F_{cr} = S^2_{res}/S^2_0$$

As $F_{cr} = 10.5429 < F_{tab} = 19.41$, the mathematical model of the suphomethylation process of nonylphenol in dimensionless system of co-ordinates adequately describes the experiment carried out. Co-ordinates of a centre of a plan in full scale ($Z^0_1, Z^0_2, Z^0_3, Z^0_4$) and variation units ($\Delta Z_1, \Delta Z_2, \Delta Z_3, \Delta Z_4$) with respect to axes Z_1, Z_2, Z_3, Z_4 were calculated as follows.

$$\left.\begin{aligned}
Z_1^0 &= \frac{Z_1^{max} + Z_1^{min}}{2} = 55 \\
Z_2^0 &= \frac{Z_2^{max} + Z_2^{min}}{2} = 45 \\
Z_3^0 &= \frac{Z_3^{max} + Z_3^{min}}{2} = 100 \\
Z_4^0 &= \frac{Z_4^{max} + Z_4^{min}}{2} = 55 \\
\Delta Z_1 &= \frac{Z_1^{max} - Z_1^{min}}{2} = 15 \\
\Delta Z_2 &= \frac{Z_2^{max} - Z_2^{min}}{2} = 7.5 \\
\Delta Z_3 &= \frac{Z_3^{max} - Z_3^{min}}{2} = 10 \\
\Delta Z_4 &= \frac{Z_4^{max} - Z_4^{min}}{2} = 15
\end{aligned}\right\} \quad (10)$$

By formula $X_j = \frac{Z_j - Z_j^0}{\Delta Z_j}$ we determine (11).

$$\left.\begin{aligned}
X_1 &= \frac{Z_1 - 55}{15} & X_2 &= \frac{Z_2 - 45}{7.5} \\
X_3 &= \frac{Z_3 - 100}{10} & X_4 &= \frac{Z_4 - 55}{15}
\end{aligned}\right\} \quad (11)$$

Then, substituting (11) into equation (5), we obtain:

$$Y_j = 105.875 - 0.375\frac{Z_1 - 55}{15} + 3.\frac{Z_2 - 45}{7.5} + 7.8125\frac{Z_3 - 100}{10} + 1.1875\frac{Z_4 - 55}{15}$$

$$+ 0.75\ \frac{Z_1 - 55}{15}.\frac{Z_2 - 45}{7.5} + 0.5625\ \frac{Z_1 - 55}{15}.\frac{Z_3 - 100}{10}$$

$$+0.1875\frac{Z_1 - 55}{15}.\frac{Z_4 - 55}{15} + 1.8125\frac{Z_2 - 45}{7.5}.\frac{Z_3 - 100}{10} + 0.6875\frac{Z_2 - 45}{7.5}.\frac{Z_4 - 55}{15} -$$

$$-3.125\frac{Z_2-100}{10}\frac{Z_4-55}{15} \qquad (12)$$

Carrying out all necessary intermediate calculations, at last we obtain:

$$Y_z = 7.814 - 1.8792\,Z_1 - 1.35972\,Z_2 - 1.01667\,Z_3 + 3.02083\,Z_4 + \\ + 0.0033\,Z_1Z_2 + 0.01708\,Z_1Z_3 + 0.00083\,Z_1Z_4 + 0.01208\,Z_2Z_3 + \\ + 0.00306\,Z_2Z_4 - 0.03125\,Z_1Z_4 \qquad (13)$$

Equation (13) is a mathematical model of the sulphomethylation process of nonylphenol in the full scale of coordinates, the estimated values (Y_z^{est}) of which are given in the last column of the table

Based on the experimental and computed values of the output parameter, the figures of the process are scheduled. As is seen from the figures obtained, the mathematical model of the process, developed in the full scale of coordinates, is in good agreement with the experimental data.

Using this mathematical model, it is possible to investigate the process in a wide range of variable parameters and to find optimum conditions for carrying out the process.

3. METHOD OF SOLUTION

While planning following the gross factor experiment (GFE), all possible combinations of factors on all chosen levels are realized. Due to optimum location of points in a factor space and linear transformation of coordinates, it is possible to eliminate the defects of a classical regression analysis, in particular the correlation between the coefficients of a regression equation. The choice of a plan is determined by the statement of the problem of investigation and the pecularities of the object. The process of investigation is usually divided into separate steps. Information obtained on each step determines further strategy of the experiment. So, the possibility of optimal control of the experiment arises. Planning the experiment allows to vary all factors simultaneously and to obtain quantative estimations of the main and interaction effects. The effects of interest are determined with less errors than using traditional methods of investigation. Ultimately, the application of the planning methods considerably increases the efficiency of the experiment

While carrying out the experiments only on two level (as in our case) with two values of factors and in so doing during the experiment all possible combinations of **k** factors are realized, then the experimental set-up following this plan is known as gross factor experiment of 2^k type. Factors levels represent the borders of the field under investigation according to the given technological parameter.

In the dimensionless coordinate system an upper level is +1, low level is -1, the coordinates of a plan's centre are equal to zero and coincide with their origin.

The planning matrix, given in Table 1 (in a dimensionless system), possesses the following properties [4]:

$$\left.\begin{aligned} &\sum_{i=1}^{N} X_{ui}X_{ji} = 0, && u \neq j;\ j = \overline{0,k};\\ &\sum_{i=1}^{N} X_{ji} = 0, && j = \overline{1,k};\ j \neq 0;\\ &\sum_{i=1}^{N} X_{ji}^2 = N, && j = \overline{0,k}. \end{aligned}\right\} \qquad (14)$$

4. RESULTS AND DISCUSSION

Following the plan Z_1, Z_2, Z_3 and Z_4 values are affected by X_1, X_2, X_3 and X_4 factors in a dimensionless coordinate system. The values of the output parameter Y^p were calculated and given in Table 1.

Thus, the mathematical model of the process in a dimensionless coordinate system was obtained. Its adequacy was checked by Fisher criterion.

Then, using an equation

$$X_j = \frac{Z_j - Z_j^0}{\Delta Z_j} \qquad (15)$$

full scale, an equation (13) was derived.

The calculated values of Y_x and Y_z models are shown in the last two columns of Table 1. As can be seen from Table 1, the mathematical model obtained adequately describes the experiment.

By means of this mathematical model, the optimal conditions for carrying out the process will be estabilished.

5. CONCLUSION

Based on planning the experiment for 4 factors, a mathematical model of sulphomethylation process of nonylphenol was developed.

The adequacy of the mathematical model was checked by Fisher criterion and will be used in the optimization process.

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Table 1. The results of planning the experiments.

Nos	Factors in Dimensionless system				Factors in full scale				Yield of HNBSA		
	X_1	X_2	X_3	X_4	Z_1	Z_2	Z_3	Z_4	Y^*	Y^P_X	Y^P_Z
1	1	1	1	1	70	60	110	70	117	120.375	119.5618
2	1	1	1	-1	70	60	110	40	125	122.5	124.8118
3	1	1	-1	1	70	60	90	70	106	102.25	104.5622
4	1	1	-1	-1	70	60	90	40	89	91.875	91.0622
5	1	-1	1	1	70	30	110	70	108	107.875	107.0618
6	1	-1	1	-1	70	30	110	40	113	112.75	115.0620
7	1	-1	-1	1	70	30	90	70	96	97	99.3122
8	1	-1	-1	-1	70	30	90	40	89	89.375	88.5622
9	-1	1	1	1	40	60	110	70	118	114.125	111.8129
10	-1	1	1	-1	40	60	110	40	114	117	117.8109
11	-1	1	-1	1	40	60	90	70	102	106.25	107.0631
12	-1	1	-1	-1	40	60	90	40	100	96.625	94.3131
13	-1	-1	1	1	40	30	110	70	104	104.622	102.3129
14	-1	-1	1	-1	40	30	110	40	110	110.25	111.0629
15	-1	-1	-1	1	40	30	90	70	105	104	104.8131
16	-1	-1	-1	-1	40	30	90	40	97	97.125	94.8131

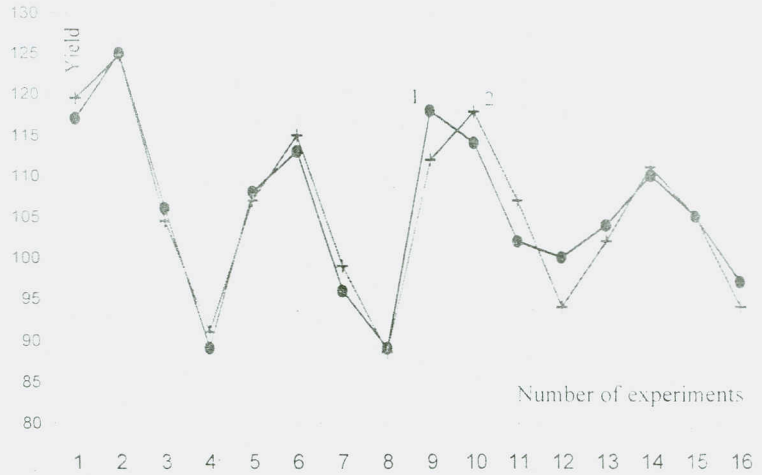

Figure 1. The sulphometulation process of nonilphenol in affinic coordinate system:
1- by experimental data;
2- by estimating the mathematical model.