

# Chlorosulfonation of Ethylic Ester of 2,4-dichlorophenoxyacetic Acid

## Mathematical modelling and optimization

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*Antifungal properties of sulfochlorides, as well as the inexpensive synthesis, require the complete study of the chlorosulfonation process. In a previous paper the results of the mathematical modelling and yield optimization were presented for the sulfochloride/ester molecular ratio  $M=7$ , and variable temperature and reaction time. In this paper, the mathematical modelling and chlorosulfonation yield optimization have been made for variable sulfochloride/ester molecular ratio and reaction time. The obtained results were compared to those previously reported and conclusions have been made on chlorosulfonation process for minimum toxicity and maximum efficiency. Thus, a maximum yield of 76% has been obtained for the following optimum values:  $M=7$ ,  $T=60^{\circ}\text{C}$  and  $t=60\text{min}$ .*

*Keywords: ethylic ester of 2,4-dichlorophenoxyacetic acid chlorosulfonation, mathematical modelling, yield optimization*

Chlorosulfonation process is well known to be toxic and the obtained sulfochloride exhibits a strong antifungal activity. This property combined with the inexpensive synthesis recommended the products for various applications, one of the most important being preservation and restoration of patrimony. In order to maximize the reaction yield and to minimize contamination hazard, the authors intended a complex and complete study on the chlorosulfonation process of ethylic ester of 2,4-dichlorophenoxyacetic acid.

In a previous paper [1], the authors reported the obtained results on establishing the influences of temperature and reaction time on chlorosulfonation yield. In the same paper the results of mathematical modelling and yield optimization were presented for a molar ratio sulfochloride/ester  $M=7$  and variable temperatures and reaction time. The established mathematical model is:

$$z = a + b \cdot x + c \cdot y + d \cdot y^2 + e \cdot y^3 \quad (1)$$

where:

$a=-52.752226$ ,  $b=1.0575$ ,  $c=1.6788262$ ,  $d=-0.0048858537$  and  $e=-8.4811412e-05$ .

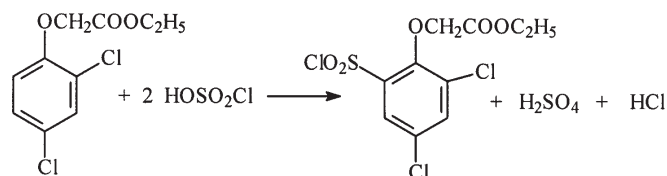
By considering the objective function described by relation (1), the optimum yield for sulfochloride was 76% and established values for the optimum of the decision variables were: temperature  $T=60^{\circ}\text{C}$  and reaction time  $t=60\text{min}$ .

In this paper, the mathematical modelling and chlorosulfonation yield optimization has been made for different values of sulfochloride/ester molar ratio and reaction time, respectively. The obtained results were then compared with those previously reported [1] and conclusions were made for the chlorosulfonation process to occur with minimum toxicity and maximum efficiency.

### Experimental part

#### Materials and methods

Experimental strategy for the chlorosulfonation process of the ethylic ester of 2,4-dichlorophenoxyacetic acid was detailed in a previous article [1]. The main reaction is:



The chlorosulfonic acid was cooled to  $15^{\circ}\text{C}$  and small amounts of ester have been added, under vigorous stirring. After the adding of ethylic ester of 2,4-dichlorophenoxyacetic acid has been completed, the temperature increased to  $50-60^{\circ}\text{C}$  and was maintained for 1 h in order to perfect the reaction. The reactants molar ratio is ester : chlorosulfonic acid = 1:6 [1].

Finally the reaction mixture was poured on ice and the precipitated product was filtered, well washed on the filter with water to eliminate the remanente acidity and then dried. The product has been purified by recrystallization from ethanol and, finally a white powder has been obtained,  $m.p.=69-70^{\circ}\text{C}$ . The structures of the ethylic ester of 5-sulfochloride-2,4-phenoxyacetic acid have been confirmed through FT-IR spectra.

### Results and discussions

Firstly, a mathematic model for the stationary regime is required to be made so that it will describe the dependency of chlorosulfonation yield on molar ratio chlorosulfonic acid/2,4-dichlorophenoxyacetic acid and reaction time [1-3]. On the basis of the previously obtained results, the experiment has been made at  $60^{\circ}\text{C}$ , obtained data being showed in table 1.

Experimental data were processed by the means of *TableCurve3D (TC3D)* programme, obtaining the response areas and then selecting the equations that best describe the studies of the system behaviour [4]. *TC3D* provided 289 equations (fig. 1) the values of the correlation coefficient being between 1 and 0.0915218.

The best equation is selected so the correlation coefficient is bigger than 0.998, and the equation must be simple in order to be easily used and the experimental points to be well framed in the response area. A batch of

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Molar ratio (M)	Time (min)	Yield (%)
3	60	28.4
5	45	58.3
5	60	64.6
7	20	41
7	35	59
7	45	69.5
7	60	75.8

**Table 1**  
YIELD VARIATION WITH MOLAR RATIO  
AND REACTION TIME

289 Equations [Rank, r <sup>2</sup> , DOF Adj r <sup>2</sup> , Fit Std Err, F-statistic, FP, Eq#, Eqn]							
File	Edit	List	Filter	Sort			
10	1	-NAN	0	1e+300	20	<b>98</b>	$z=a+bx+c(\ln x)^2+d\ln y+e(\ln y)^2+f(\ln y)^3$
11	1	-INF	1.579e-14	1.168e+30	31	<b>2046</b>	$z=a+bx+cx^2+\text{LOGISTIC}(d,e,f)$
12	1	-INF	2.588e-12	4.918e+25	27	<b>2058</b>	$z=a+bx+cx^2+\text{EXTRVAL}(d,e,f)$
13	1	-INF	8.496e-11	4.562e+22	31	<b>2034</b>	$z=a+bx+cx^2+\text{LOGNORM}(d,e,f)$
14	1	-INF	4.134e-11	1.927e+23	12	<b>2022</b>	$z=a+bx+cx^2+\text{LORY}(d,e,f)$
15	1	-INF	1.553e-12	1.365e+26	19	<b>2010</b>	$z=a+bx+cx^2+\text{GAUSSY}(d,e,f)$
16	1	-NAN	0	1e+300	35	<b>896516</b>	$z=a+bx^0.5+cx+d(\ln y)^2+e\ln y+f\ln y^2$
17	1	-NAN	0	1e+300	38	<b>945021</b>	$z=a+bx+ce^{-x}+d(\ln y)^2+e\ln y+f\ln y^2$
18	1	-NAN	0	1e+300	41	<b>913362</b>	$z=a+bx^0.5+cx^2+d(\ln y)^2+e\ln y+f\ln y^2$
19	1	-NAN	0	1e+300	44	<b>950722</b>	$z=a+bx^0.5+ce^{-x}+d(\ln y)^2+e\ln y+f\ln y^2$
20	1	-NAN	0	1e+300	39	<b>928287</b>	$z=a+bx+c\ln x^2+d(\ln y)^2+e\ln y+f\ln y^2$
21	1	-INF	8.896e-14	4.161e+28	17	<b>2118</b>	$z=a+bx+cx^2+\text{SIGY}(d,e,f)$
22	1	-INF	1.145e-12	2.51e+26	18	<b>2094</b>	$z=a+bx+cx^2+\text{LORCUMY}(d,e,f)$
23	1	-INF	3.46e-14	2.75e+29	61	<b>2106</b>	$z=a+bx+cx^2+\text{LNCUMY}(d,e,f)$
24	1	-INF	5.96e-08	9.268e+16	11	<b>168</b>	$z=a+bx+cy^2+dy+ey^2+fy^3$
25	1	-INF	8.429e-08	4.634e+16	16	<b>103</b>	$z=a+bx+c(\ln x)^2+dy+ey^2+fy^3$
26	1	-INF	9.424e-08	3.707e+16	15	<b>93</b>	$z=a+bx+c(\ln x)^2+dy+ey^2+fy^3$
27	1	-INF	9.424e-08	3.707e+16	10	<b>18</b>	$z=a+bx+cx^2+dy+ey^2+fy^3$
28	1	-INF	1.264e-07	2.059e+16	12	<b>178</b>	$z=a+bx+cy^2+dy+ey^2+fy^3$
29	0.9999291	-INF	0.341669	2820.2721	15	<b>2017</b>	$z=\text{LORX}(a,b,c)+\text{LORY}(d,e,f)$
30	0.999855	-INF	0.4886545	1378.6986	44	<b>2038</b>	$z=a+\text{LOGISTIC}(b,c,d)+\text{LOGISTIC}(1,e,f)$
31	0.9998333	-INF	0.5237894	1199.9059	41	<b>152158560</b>	$\ln z=a+bx+c\ln x^2+d\ln y+e\ln y+f\ln y^2$
32	0.9998333	-INF	0.5237894	1199.9059	41	<b>152097487</b>	$\ln z=a+b\ln x+cx^0.5+dy+ey^1.5+f\ln y^2$
33	0.9998333	-INF	0.5237894	1199.9059	39	<b>152176709</b>	$\ln z=a+bx+ce^{-x}+dy+ey^1.5+f\ln y^2$
34	0.9998333	-INF	0.5237894	1199.9059	41	<b>152124428</b>	$\ln z=a+b\ln x+cx^1.5+dy+ey^1.5+f\ln y^2$
35	0.9998333	-INF	0.5237894	1199.9059	41	<b>152138897</b>	$\ln z=a+b\ln x+cx^2+dy+ey^1.5+f\ln y^2$
36	0.9998333	-INF	0.5237894	1199.9059	36	<b>152127518</b>	$\ln z=a+bx^0.5+cx+dy+ey^1.5+f\ln y^2$
37	0.9998333	-INF	0.5237894	1199.9059	45	<b>152145189</b>	$\ln z=a+b\ln x+ce^{-x}+dy+ey^1.5+f\ln y^2$
38	0.9998333	-INF	0.5237894	1199.9059	43	<b>152144693</b>	$\ln z=a+bx^0.5+c\ln x^2+dy+ey^1.5+f\ln y^2$
39	0.9998333	-INF	0.5237894	1199.9059	38	<b>152136467</b>	$\ln z=a+bx^0.5+cx^1.5+dy+ey^1.5+f\ln y^2$
40	0.9998333	-INF	0.5237894	1199.9059	41	<b>152159119</b>	$\ln z=a+bx^0.5+ce^{-x}+dy+ey^1.5+f\ln y^2$

Fig. 1. List of the equations that describe the dependency of the yield with molar ratio and reaction time.

Rank 27 Eqn 18 $z=a+bx+cx^2+dy+ey^2+fy^3$					
r <sup>2</sup>	Coef Det	DF Adj r <sup>2</sup>	Fit Std Err	F-value	
1		-INF	9.424322e-08	3.707087e+16	
Parm	Value	Std Error	t-value	95% Confidence Limits	
a	-120.655	1.90321e-08	-8.3398e+07	-120.655024	-120.654976
b	43.1	2.39116e-07	1.80247e+08	43.09999696	43.10000304
c	-3.125	2.28127e-08	-1.3699e+08	-3.12500029	-3.12499971
d	0.006	1.5176e-07	39536.10611	0.005998072	0.006001928
e	0.042	4.03672e-09	1.04045e+07	0.041999949	0.042000051
f	-0.00048	3.30971e-11	-1.4503e+07	-0.00048	-0.00048
X at Fn Zmin	Y at Fn Zmin	Fn Zmin			
3	60	28.4			
X at Fn Zmax	Y at Fn Zmax	Fn Zmax			
7	60	75.8			
Procedure GaussElim					
r <sup>2</sup>	Coef Det	DF Adj r <sup>2</sup>	Fit Std Err		
1		-INF	9.424322e-08		
Source	Sum of Squares	DF	Mean Square	F Statistic	P>F
Regr	1646.2771	5	329.25543	3.70709e+16	0.00000
Error	8.8817842e-15	1	8.8817842e-15		
Total	1646.2771	6			
X Variable:					
Xmin:	3	Xmax:	7	Xrange:	4
Xmean:	5.8571428571	Xstd:	1.5735915849		

Fig. 2. Results for the analysis of model equation 2

42 equations was retained, and from them, on the reason of the statistic parameters of the application (fig. 2) the following equation was chosen:

$$z = a + b \cdot x + c \cdot x^2 + d \cdot y + e \cdot y^2 + f \cdot y^3 \quad (2)$$

Coefficient values are: a = -120.655, b = 43.1, c = -3.125, d = 0.006, e = 0.042, f = -0.00048.

The response area described by the equation (2) is showed in figure 3.

The analysis of the modelling adavance [2,3] has been made by the means of Fisher and Student tests, showed in figure 2.

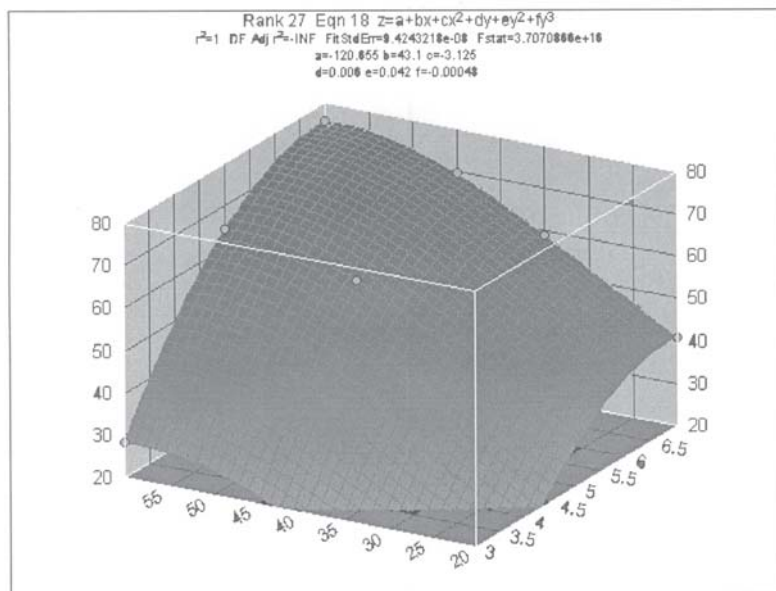


Fig. 3. Response area described by the equation (2)

XYZ	X Value	Y Value	Z Value	Z Predict	Residual	Residual%	95% Confidence Limits	95% Prediction Limits
1	3	60	28.4	28.4	-4.42e-16	-1.56e-15	28.399999 28.400001	28.399998 28.400002
2	5	45	58.3	58.3	2.637e-16	4.523e-16	58.299999 58.300001	58.299998 58.300002
3	5	60	64.6	64.6	6.731e-16	1.042e-15	64.599999 64.600001	64.599998 64.600002
4	7	20	41	41	-4.18e-17	-1.02e-16	40.999999 41.000001	40.999998 41.000002
5	7	35	59	59	3.286e-16	5.586e-16	58.999999 59.000001	58.999998 59.000002
6	7	45	69.5	69.5	-5.69e-16	-8.19e-16	69.499999 69.500001	69.499998 69.500002
7	7	60	75.8	75.8	-1.53e-16	-2.01e-16	75.799999 75.800001	75.799998 75.800002

Fig. 4. Experimental data, estimated values, residue and reliability range

Precision	Avg Abs Error	Min Abs Error	Max Abs Error
18	1.109848e-17	1.098506e-18	5.814034e-17
17	1.955936e-16	8.019071e-17	7.296881e-16
16	2.800382e-16	3.142048e-17	1.576159e-15
15	1.269161e-15	4.940154e-16	3.20707e-15
14	1.256687e-15	4.89192e-16	3.175764e-15
13	1.256687e-15	4.89192e-16	3.175764e-15
12	1.628113e-17	5.150898e-19	5.068645e-17
11	1.628113e-17	5.150898e-19	5.068645e-17
10	1.628113e-17	5.150898e-19	5.068645e-17
9	1.628113e-17	5.150898e-19	5.068645e-17
8	1.628113e-17	5.150898e-19	5.068645e-17
7	1.628113e-17	5.150898e-19	5.068645e-17
6	1.628113e-17	5.150898e-19	5.068645e-17
5	0.0001896204	6.596306e-05	0.00078125
4	0.0017065833	0.0005936675	0.00703125
3	0.009451661	0.0013192612	0.046875
2	0.0275723751	0.0127922041	0.090625

Removing	Avg Abs Error	Min Abs Error	Max Abs Error
a	4.5757290498	1.5917546174	18.85234375
b	6.6497325989	3.4838337182	20.203125
c	2.2700901396	0.9903169014	4.39453125
d	0.0074768257	0.0029268293	0.01875
e	2.1552694647	0.4097560976	5.323943662
f	1.1888819221	0.0936585366	3.6507042254

Fig. 5. Medium, minimal and maximal absolute errors for the experimental data and model coefficients

In figure 4 are presented the statistic parameters [4-6] that helped to appreciate the performances of the model and comparison of the experimental values with those estimated by the model.

On this purpose the medium, minimal and maximal errors for the experimental data and model coefficients were analyzed (fig. 5).

In order to view the optimum, a nonlinear optimization problem has been made, in which the objective function was the global yield characterized by equation 2. Decision variable were: molar ratio chlorosulfonic acid/ 2,4-dichlorophenoxyacetic ester and reaction time. The restrictions imposed by reaction occurrence were: yield  $\eta \leq 76\%$ , reaction time  $t \geq 50$  min and molar ratio  $M \leq 7$ , at a

temperature of  $T=60^\circ\text{C}$  and taking into consideration the results obtained in article [1]. In those conditions the optimum yield was 76% at  $M = 6.9$  and  $t = 60$  min.

Stability analysis for the optimum (fig. 6) has been made by simulation with the mathematic model described by equation 2.

It must be highlighted the fact that for  $T=60^\circ\text{C}$ , the optimum is maintained for a reaction time that could vary with  $\pm 5$  min. The second parameters, the molar ratio chlorosulfonic acid/ 2,4-dichlorophenoxyacetic ester is recommended to be maintained at 6.9. The variation of the ratio with  $\pm 10\%$  has a piffling influence on the optimum value. The increase of the ratio over 7, even with 10% decrease the yield with 2%.

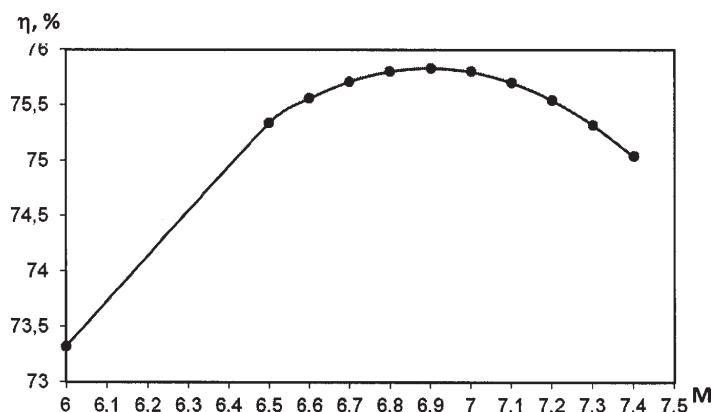


Fig. 6. Influence of the molar ratio chlorosulfonic acid/ 2,4-dichlorophenoxyacetic ester on chlorosulfonation yield

## Conclusions

A mathematical model for the chlorosulfonation process of the 2,4-dichlorophenoxyacetic acid ethylic ester in stationary regime has been obtained and describes the dependency of reaction yield with molar ratio chlorosulfonic acid/ester and reaction time, respectively, as a polynomial of 3<sup>rd</sup> degree, the correlation coefficient being 1, so the correlation is perfect.

The accuracy of the model estimations have been studied by the means of statistic parameters, such as: medium, minimal and maximal values for absolute errors and experimental values of *Student*, *Fisher* tests, residues, standard deviation, and reliability range limits.

Relative to the previous mathematical modelling, that studied the dependency of the global yield with temperature and reaction time, the same type of equation has been obtained, but with different coefficient values. Correlation coefficient and statistic parameters showed that the model described by the selected equation is more exact.

Mathematical model obtained has been used to optimize the yield, using as decision variables molar ratio chlorosulfonic acid /ester and reaction time. The values for the optimum yield and optimum for the decision variables are close to those previously obtained.

Optimum stability analysis showed that a variation of reaction time with  $\pm 5$  min has no effect. But it is recommended to strictly maintain the molar ratio

chlorosulfonic acid/ester at 6.9, bigger values decreasing proportionally the yield.

So, in order to occur chlorosulfonation with minimum toxicity and maximum efficiency (76%), the optimum operating parameters will be molar ratio chlorosulfonic acid/ 2,4-dichlorophenoxyacetic ester  $M=7$ , temperature  $T=60^{\circ}\text{C}$  and reaction time  $t=60\text{min}$ .

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