

# **THE MODELLING OF CHROMATOGRAPHIC EXTRACTION OF CERTAIN ORGANIC DISSOLVENTS IN THE PROCESS OF WASTEWATER PURIFICATION WITH MULTICOMPONENT POLLUTION**

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*The mathematical model of chromatographic extraction of certain organic dissolvents for the normal phases with changeable content of the mobile phase was developed and its adequacy to the real process was proved*

## **THE PROBLEM DESCRIPTION.**

The effective method of wastewater purification from the organic dissolvents is their adsorption on the natural or artificial sorbents. But in case of presence of few dissolvents at a time in the wastewater this process is complicated because in this case the adsorbed molecules of one dissolvent can be forced out by the molecules of the other one and go to the solution again. The process of chromatography can be effective, because it allows not only to purify the wastewater from dissolvents mixture, but to receive some certain pure dissolvents that can be used in a technological process.

## **THE ANALYSIS OF RECENT RESEARCHES AND PUBLICATIONS.**

The processes of chromatography are modeled on the base of a certain estimations and are described by a theoretical models. Chromatographic splitting is usually performed under the isometric conditions, that is under the constant temperature, pressure or under the constant content of a mobile phase during the process. But the changes of these parameters can significantly affect the adsorption processes in multicomponent systems. The changeable adsorption conditions are used in the reverse adsorption processes under the high pressures during the processes of waste purification [1,2]. In the liquid chromatography the adsorption conditions with a changeable content of a mobile phase studying is often used to improve the process of chromatographic splitting.

The changeable mobile phase content for the normal phase systems is complied to the conditions of linear isotherm and is described on the base of theoretical adsorption model [3-6]. In these models the adsorption on the polar adsorption surface is explained as competitiveness between the solution molecules and modifier on the adsorption centers.

The simplest model was suggested in [7], with a name “competitive Langmuira isotherm”, for the calculation of adsorption balance in the binary scheme (solution – modifier). If the coefficients of “dissolvent – modifier” isotherm are known, then the coefficients of the “solution – modifier” competitive isotherm can be calculated under the certain modifier concentrations.

For modeling of the chromatography process there are also widely used bi-Langmuira and Unilana models[8].

In heterogeneous adsorption model (HIAS) which was developed in [9], the adsorbent surface is presented with a consideration of adsorption centers activity. This approach requires the range of controlled parameters, and also the energy calculation on the adsorbing surface.

**Aim of the work:** To develop the technological process mathematical model of chromatographic splitting of organic dissolvents, which appear to be contained in the wastewater with multi-component pollution; to carry out the experimental investigation of the process and to prove the adequacy of the mathematical model to the real process.

**Mathematical model of the process:** For mathematical modeling of the balance between the component concentration in mobile and fixed phases it is necessary to foresee the differential mass balance of the one and  $i$  component in the mobile phase:

$$\frac{\partial c_i^m}{\partial t} + F \frac{\partial \Gamma_i^*}{\partial t} + \omega \frac{\partial c_i^m}{\partial z} = D_a \frac{\partial^2 c_i^m}{\partial z^2} \quad (1)$$

where  $\omega = u / \varepsilon_t$  - speed in the thinnest cutover;  $\varepsilon_t$  - the total porosity of a tower;  $D_a$  - a coefficient of dispersion connected with the tower effectiveness,  $N = \omega L / 2D_a$ ;  $c_i^m$  - the component concentration in the mobile phase;  $t, z$  – coordinates of the time and area,  $\Gamma_i^*$  - the additional adsorption in a balance with  $c_i^m$ .

The additional adsorption for the mixture of a component in the adsorption tower of mobile phase (modifier) and inert phase are described with the equation (2):

$$\Gamma_A^* = q_A^* - q_A^* \cdot x_A^m = q_A^* (1 - x_A^m) \quad (2)$$

For the solution with the stated concentration  $\Gamma_i^* \cong q_i^*$ .

The calculation in mole fraction according to the formula (1) we will receive:

$$\frac{\partial x_i^m}{\partial t} + F \frac{\partial \Gamma_i^*}{\partial t} \cdot \frac{M^m}{\rho^m} + \omega \frac{\partial x_i^m}{\partial z} = D_a \frac{\partial^2 x_i^m}{\partial z^2} \quad (3)$$

where  $M^m$  i  $\rho^m$  - the equivalent mole mass and density of the mobile phase;

$$M^m = f(x_i^m), \quad \rho^m = f(x_i^m).$$

To describe the chromatographic process the boundary conditions of Danckwerts-type are used, for which:

$$t > 0; \quad z = 0$$

$$u(x_i, F(t) - x_i^m(t, 0)) = -D_a \frac{\partial x_i^m(t, 0)}{\partial z} \quad (4)$$

where  $x_i, F(t)x$  - determines the profile of a sample impulse.

Then we receive:

$$x_i, F(t) = \begin{cases} x_{i,F} & \text{for } t \in [0, t_p] \\ 0 & \text{for } t > t_p \end{cases} \quad (5)$$

The determination of an additional adsorption was carried out with the use of impulse method. Under this method, at first the tower is balanced in a certain concentration level, and then the impulse was created in order to make additional stimulation. As soon as the difference between the equilibration concentration and response concentration is not significant, the tower stayed in the equilibration. The mathematical analysis was based on the principles of classical equilibration theory.

The equilibration theory in the processes of chromatography is described by the ideal model, which considers the balance between the component concentrations in the mobile and fixed phase and ignores axial dispersion and kinetic effects. The ideal model can be presented by the equation (3), ignoring the dispersion. After the transformations for the  $i$  standard component we receive:

$$\frac{\partial x_i^m}{\partial t} + \left( \frac{\omega}{1 + F(d\Gamma_i^* / dx_i^m)(M^m(x_i^m) / \rho^m(x_i^m))} \right) \frac{\partial x_i^m}{\partial z} = 0 \quad (6)$$

The time of the stimulation introduction is described as:

$$t_{\Gamma i}(x_i^m) = t_{\Gamma 0} \left( 1 + F \frac{d\Gamma_i^*}{dx_i^m} \frac{M^m(x_i^m)}{\rho^m(x_i^m)} \right) \quad (7)$$

where  $t_{\Gamma 0} = \frac{L}{\omega}$  - time before the stimulation introduction (in other words, the tower idle time)

under the tower length  $L$ .

The dependence (7) can be used for the calculation of the additional adsorption of the component  $i = A$  with taking to consideration the formula (2):

$$\Gamma_A^* = \int_0^{x_A} \left( \frac{t_{\Gamma}/t_{\Gamma 0} - 1}{F} \right) \frac{\rho^m(x_i^m)}{M^m(x_i^m)} dx_A \quad (8)$$

or:

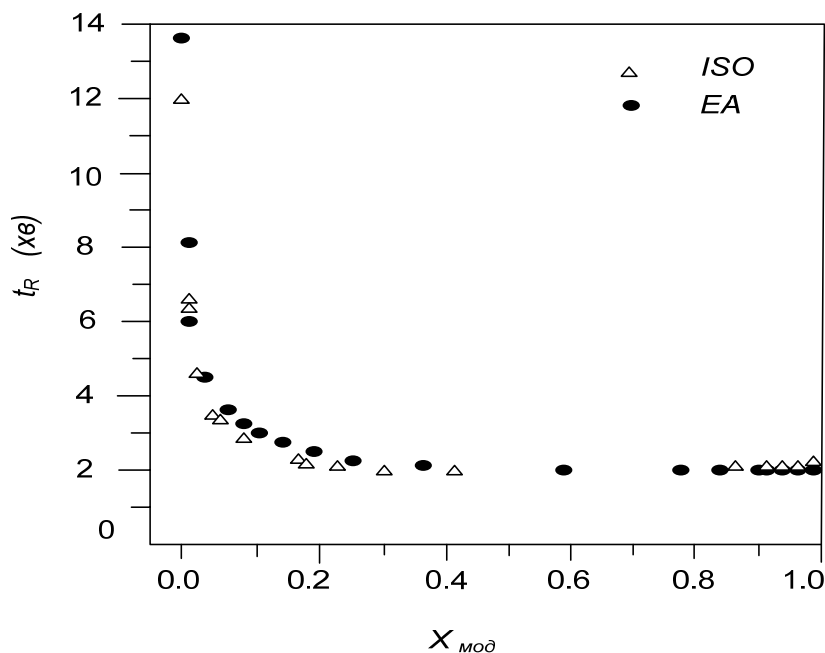
$$\Gamma_A^* = \int_0^{x_A} \left( \frac{t_{\Gamma}/t_{\Gamma 0} - 1}{F} \frac{\rho^m(x_i^m)}{M^m(x_i^m)} dx_A \right) \quad (9)$$

In the equations (8) and (9)  $\Gamma_A^*$  - is the additional adsorption, corresponding to the adsorbent volume (for example mole/cm<sup>2</sup> of the adsorbent).

### THE EXPERIMENTAL RESEARCH.

For the researches the liquid chromatograph HPLC LaChom MERCK was used. The experiment took place with the tower saturation by polar solvent (ethyl acetate or isopropanol). The tower length and diameter are 250mm and 4mm respectively, which is filled with silica LiChrospher® Si 60 with a pore diameter 60 Å, the particles size 5 μm, produced by Merck, Darmstadt, Germany. In order to determine the adsorption isotherms, the tower was balanced for the each concentration of standard mixture, in other words until the receiving of horizontal line on the detector, which characterizes the saturation of adsorbed substance of a certain concentration by the mobile phase component, the impulse was put with a small excess of the concentration.

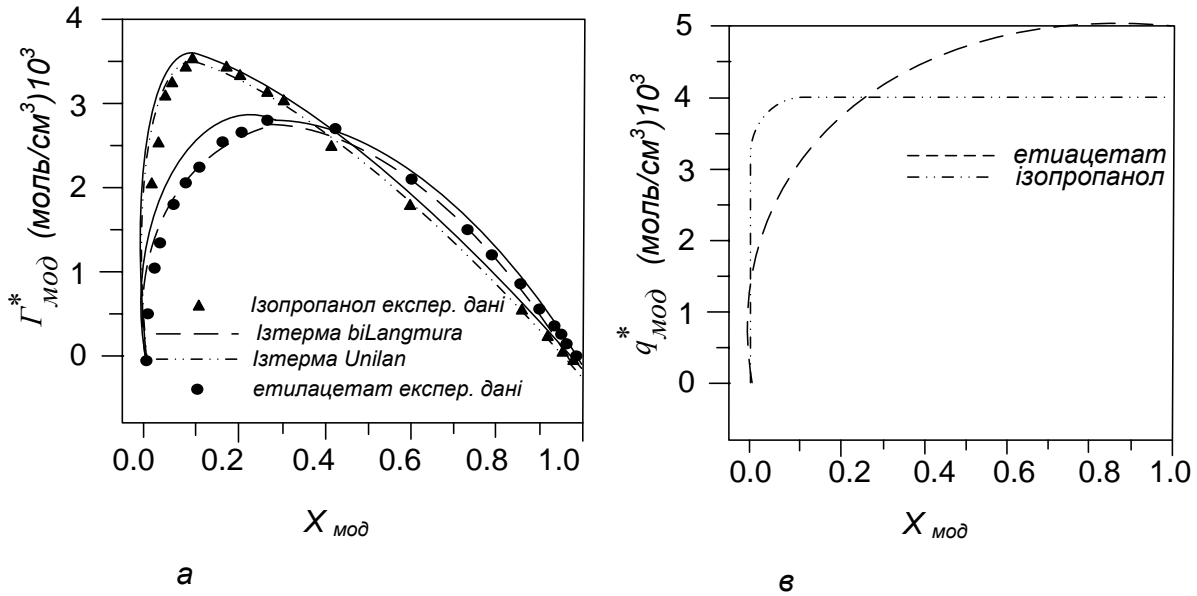
**The results discussion.** On the Figure 1it is presented the time of modifier impulses appearance with a dependence from a mole part of the mobile phase.



**Figure 1.** The analysis of the impulse results for the systems: ethyl acetate (EA) –n-hexane and 2-propanol (ISO) –n-hexane

The corresponding additional adsorption is described in the Figure 2a. According to the measurements of impulses appearance time for the pure n-hexane and for 2-propanol (ISO), the excessive adsorption was calculated with the use of the equation (9).

The adsorption data, described in the Figure 2a and 2b show that the surface is saturated by more polar modifier (so is ISO) under the relatively low concentration in the mobile phase. Besides, due to ISO activity the polarity is not ideal in the mobile phase, which contains n-hexane and which impacts significantly on the adsorption.



**Figure 2.** The adsorption in the systems: ethyl acetate (EA) –n-hexane and ISO (isopropanol)- n-hexane: (a) the excessive adsorption; (b) the correspondence of adsorption isotherms.

The set of experimental data of the excessive adsorption, presented on the Figure 2a is used to determine the parameters of the models:

bi-Langmuira:

$$\Gamma_A^* = \left( \frac{q_{A1}^\infty \cdot K_1 \cdot x_A^m \cdot \gamma_A^m}{1 + K_1 \cdot x_A^m \cdot \gamma_A^m} + \frac{q_{A11}^\infty \cdot K_{11} \cdot x_A^m \cdot \gamma_A^m}{1 + K_{11} \cdot x_A^m \cdot \gamma_A^m} \right) (1 - x_A^m) \quad (10)$$

Unilan:

$$\Gamma_A^* = \left[ \frac{q_A^\infty}{2h} \ln \left( \frac{1 + q_A^\infty \cdot K \cdot x_A^m \cdot \gamma_A^m \cdot \exp(h)}{1 + K \cdot x_A^m \cdot \gamma_A^m \cdot \exp(-h)} \right) \right] (1 - x_A^m) \quad (11)$$

The isotherm model is connected with the respective dependences  $\gamma_A^m = f(x_A^m)$  (A-modifier = EA or ISO). The parameters for bi-Langmuir and Unilan models are presented in the Table 1, the theoretical excessive adsorption is presented in the Figure 2a. The both models reflect the adsorption data for EA with an authentic accuracy, but bi-Langmuir model is more accurate for the ISO. The adsorption isotherms are described on the Figures 2a and 2b respectively.

Apparently, bi-Langmuir model characterizes two energetically different adsorption centers, which are differentiated by low and high equilibration constant. The model of two centers can be set equal to the average values of energetic constants of homogeneous surface  $K_I$ ,  $K_{II}$ .

It should be pointed out that the phenomenon of EA saturation possibility with not significant coefficient (center I) is more higher than for the ISO, which can be explained as a model inaccuracy for the two centers. For Unilan model the saturation possibilities for all the components were more accurate, and  $q_i^\infty$  number was proximate to the experimental data.

Table 1. The parameters for bi-Langmuir and Unilan models.

Component	ethyl acetate EA (modifier)	2-propanol ISO (modifier)
Isotherm bi-Langmuir - equation (10)		
$q_{il}^{\infty}$	0.0133	0.0025
$K_{il}$	0.448	0.504
$q_{iII}^{\infty}$	0.00142	0.0034
$K_{iII}$	25.276	16.44
RSS	$5.85 \times 10^{-8}$	$3.2 \times 10^{-7}$
Isotherm Unilan - equation (14)		
$q_i^{\infty}$	0.0059 <sup>a</sup>	0.0059 <sup>a</sup>
$K_I$	3.40	4.366
$h_i$	0.873	3.038
RSS	$3.83 \times 10^{-8}$	$4.7 \times 10^{-7}$

RSS: the remaining sum of quadratic deviations between the theoretical and experimental excessive adsorption.

## CONCLUSIONS.

The results of experimental chromatogram comparing under the different modifier concentrations in the mobile phase with the theoretical showed the compliance between the theoretical and experimental profiles. Under the conditions of low modifier concentrations there can be observed the significant deviations between the experimental and theoretical data. For the standard conditions of chromatography under the high concentrations, the excesses modifier regarding to the solution the calculated model is effective; but the ideal compliance between the theoretical and experimental profiles is not being achieved. The method can be used to estimate the action of solution adsorption when the other dissolvents are present and their adsorption balance is known. The successful experimental examination showed the model compliance for the standard equilibration component part and model of foreseeing for double equilibration of modification solution.

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