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PROPERTIES OF ISOCHRONES AS PARAMETERS OF A NEW TYPE IN THE KINETIC MODEL OF COMPLEX CHEMICAL PROCESSES

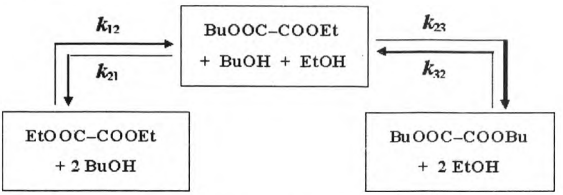
SUMMARY. The paper presents a new type of parameters of kinetic models for complex chemical processes based on the analysis of the isochrone geometry of the system trajectory chart. The earlier experimental data on kinetics of the re-etherification process in the chemical system containing three esters, two alcohols, and a catalyst (diethyl oxalate, ethyl butyl oxalate, dibutyl oxalate, ethanol, butanol, n-toluene sulfonic acid) are used for the analysis. The data are processed by mathematical methods to draw the isochrones (an isochrone is a curve connecting the points of all the trajectories corresponding to the same time interval passed from the start of the reaction). The isochrone geometry in the space of states is modeled by the equations of conic curves. All the isochrones appear to be segments of ellipses. Some mathematical parameters of isochrones, A (invariant, large and minor determinants, semi-axes, etc.) are calculated.

The dependence of these parameters on time (A = f(t)) is investigated, and the regularity of time evolution of these parameters is demonstrated. It is concluded that the use of such properties as the parameters of the kinetic models of the complex chemical system is allowable.

KEY WORDS. Chemical process, re-etherification, oxalates, kinetics, trajectory chart, isochrones, parameters of kinetic models.

Introduction. The high efficiency of modern chemical technology is largely caused by the theoretical achievements in the field of chemical kinetics. In its turn, the successful development of chemical kinetics as a branch of physical chemistry is closely related to the use of mathematical models. In this respect, the vector space model –"the space of structures" (SS) – is one of the most promising ones. In the context of this model, all the possible states (compositions) of the chemical system can be represented as a topologically ordered set of "state vectors" taking the form: $n = (n_1, n_2, ..., n_k)$, where n_i is the number of moles of the i^{th} compound. All chemical processes in such a system can be represented as smooth curves – "stoichiometric trajectories" – taking the form: $F(n_1, n_2, ..., n_k)$=const [1-3]. The "trajectory chart" as the set of such trajectories is an important and useful property of the kinetic behavior the chemical system under study demonstrates. This kind of kinetic models has significant advantages. Firstly, in the SS, the set of geometric parameters (length, curvature, inflections, extremes, etc.) can be associated with the shape of the trajectories [4-6]. Secondly, in the SS, the velocity vector fields (V = dn/dt) and chemical affinity forces (A = - grad G) can be determined [7-9]. The features of the trajectories and the vector fields (divergence, curl, etc.) may be used as a new type of kinetic parameters, e.g. Div V = f(t), or V = f(A).

In [10], the authors present the experimental data for the dialkyloxalate re-etherification reaction proceeding in accordance with the scheme below, the experimental procedure is also described.



The kinetic results are presented as a set of points arranged in a two-dimensional simplex of the three-dimensional space of compositions (Fig. 1). The total of 330 points lying on 30 trajectories is determined, the beginnings of theses curves correspond to three pure substances (DEO – diethyloxalate, EBO – ethyl butyl oxalate, and DBO – dibutyl oxalate) and their binary mixtures.

In [11], the method of mathematical processing of the experimental data array is described; it enables this array to be approximated by means of the formal kinetic model:

Scheme 1

$da/dt = -k_{12} \cdot a \cdot d + k_{21} \cdot b \cdot e$

$db/dt = k_{12} \cdot a \cdot d - k_{21} \cdot b \cdot e - k_{23} \cdot b \cdot d + k_{32} \cdot c \cdot e$

$dc/dt = k_{23} \cdot b \cdot d - k_{32} \cdot c \cdot e$

(a, b, c, d, e are the current concentrations of DEO, EBO, DBO, butanol, and ethanol, respectively) and the set of the rate constants for all the elementary reactions to be determined. The optimized values of the rate constants are equal ($mol^{-1} \cdot l^2 \cdot s^{-1}$):

$k_{12} = 2.774 \cdot 10^{-4}$; $k_{21} = 1.106 \cdot 10^{-4}$; $k_{23} = 1.114 \cdot 10^{-4}$; $k_{32} = 1.936 \cdot 10^{-4}$

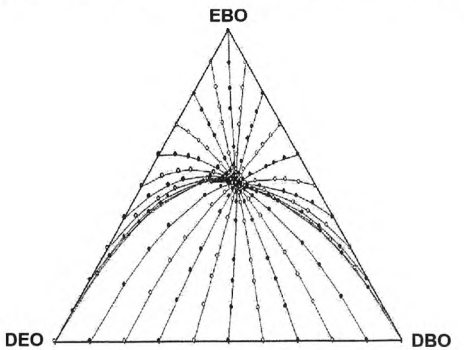


Fig. 1. The experimental kinetic trajectories for the process of the re-etherification of three dialkyloxalates [1]

Within the model obtained, the trajectory-isochronous chart is constructed; it gives a complete picture of kinetics of chemical process involving the simultaneous occurrence of several elementary reactions (Fig. 2).

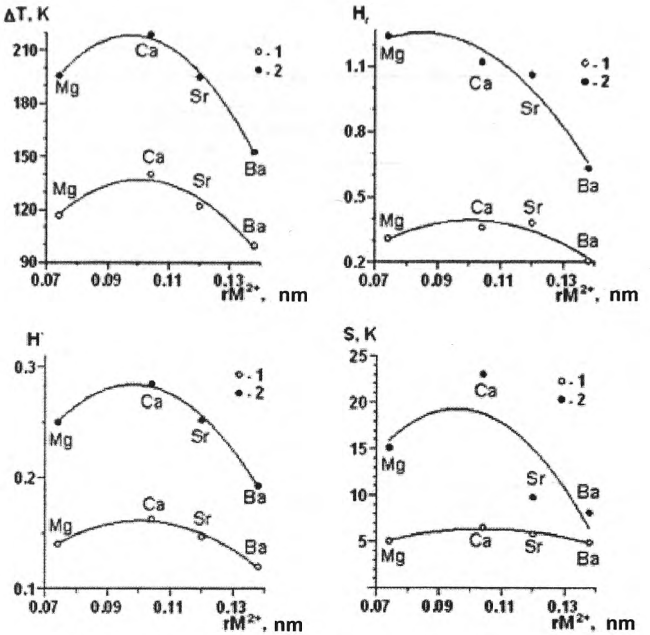


Fig. 2. The trajectory-isochronous chart for the system with dialkyloxalate re-etherification reactions

The purpose of this paper is to study the isochrone geometry as the curves connecting the points of all the trajectories corresponding to the same time interval passed from the start of the reaction.

Results and discussion. The isochrones being the time representations of the bottom side of the composition triangle (t=5, 10, 15, 30, 45, 60 minutes) were selected for study, since their geometrical parameters are explicit and can be approximated quite accurately by algebraic equations.

As the approximation model, the coordinates of 30 equidistant points for each of the six isochronous were calculated according to Scheme 1. Conic curves (an ellipse, a parabola, and a hyperbola) were selected as the approximation model.

With a compiled computer program, we could determine the type of a curve and a number of its mathematical parameters: the invariant, the large and small determinants, the semi-invariant, the proper values, the semi-axes, the compression ratio, the eccentricity, the parameter, the distance to the directrix, the center coordinates, the x-axis tilt angle [12].

The results of the approximation of isochrones by the conic curves given in Table. 1 demonstrate that: a) in all the cases, the approximating curve is a segment of an ellipse (the eccentricity $\varepsilon<1$), b) there is a certain dependence of the ellipse mathematical parameters on time.

Table 1

The values of the mathematical parameters of the isochrones approximated by the conic curves (the ellipse)

Time, min.	5	10	15	30	45	60
Invariant	1.44	1.62	1.71	1.80	1.82	1.11
Large determinant	0.43	0.59	0.65	0.65	0.56	0.07
Small determinant	-435	-385	-265	-60	-11	-0.28
Semi-invariant	455	1,980	2,900	3,740	3,390	433
λ1 proper value,	1.02	1.08	1.15	1.31	1.43	1.04
λ2 proper value	0.42	0.55	0.56	0.49	0.39	0.07
a-semi-axis	49.0	34.7	27.0	13.7	7.28	7.51
b-semi-axis	31.6	24.7	18.8	8.45	3.79	1.94
Compression ratio	0.64	0.71	0.70	0.62	0.52	0.26
Eccentricity	0.76	0.70	0.72	0.79	0.85	0.97
Focal parameter	20.4	17.6	13.1	5.20	1.97	0.50
Distance to the directrix	26.6	25.0	18.3	6.59	2.31	0.52
X-coordinate of the center	58.9	59.3	59.8	60.6	60.7	60.8
Y-coordinate of the center	31.5	40.7	44.6	48.6	49.8	48.7
X-axis tilt angle	9.38	22.4	30.6	38.0	40.1	11.1

The dependence of several parameters on time is rather clear (Fig. 3).

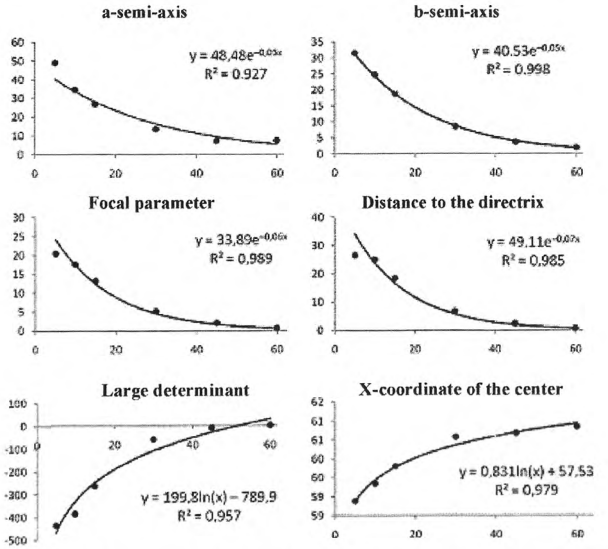


Fig. 3. The dependences of the parameters of the approximating curve (ellipse) on time (the X-axis, min.)

Conclusion.

1. The graphs (Fig. 3) demonstrate that a number of properties of the approximating curve (the ellipse) regularly vary with time and may be considered as the parameters of the kinetic models. As for the other properties, their dependence on time is expressed in a less regular form, which can be explained by the occurrence of errors in the input data.

2. All the dependences (Fig. 3) have an exponential form peculiar to relaxation processes. This fact confirms that the properties described are not formal but they meaningfully represent the relaxation nature of chemical transformations.

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