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Uncertainty and Invariants of Inverse Problem Solutions for a First-Order Reaction

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Abstract—The problem of uncertainty of inverse problem solution for a first-order reaction with rate constant distribution of reactive states is considered. Although every distribution determines the reaction kinetics unambiguously, the inverse problem solving recovers a set of distributions in accordance with the same kinetic data. A choice of one of them is shown to be impossible in principle because all distributions give the same description of the reaction kinetics, and uncertainty of the solution remains even if the accuracy and number of measurements are increased many times. A method for the calculation of a set of distributions is proposed. The method can be applied to systems with both discrete and continuous sets of states. The distributions belonging to the set of inverse problem solutions are shown to have invariants, which can be determined from the initial moments of normalized distributions or directly from data on the reaction kinetics. The physical meaning of the invariants is considered as statistical rate constants for states with high, medium, and low reactivities that characterize the width of the true distribution and the degree of its asymmetry. The application of the invariants is considered for particular examples of the fluorescence decay of Rhodamine 6G in porous glasses and of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin in the Langmuir–Blodgett layers. Despite uncertainty of the inverse problem solution, the application of the invariants gives rise to unambiguous characteristics of the reactivity of compounds in reactions with distributed parameters.

INTRODUCTION

A kinetic curve of first-order reactions often differs from an exponential curve; it is characterized by the reactivity distribution and can be represented by the sum of two or more exponentials. Such a multiexponential kinetics is typical of not only multicomponent reactions like, for example, the fluorescence of a mixture of fluorophores or the radioactive decay of a mixture of isotopes. It is inherent in heterogeneous reactions [1], reactions in polymers [2] and organic glasses [3], and reactions in an organized molecular environment, which have recently attracted great attention. These are, for example, porphyrin fluorescence in the Langmuir–Blodgett layers [4]; the reactions of benzophenone included in the cyclodextrin ring [5]; and reactions in polymeric microblocks [6], complexes with polynucleotides [7], membranes [8], micelles [9], vesicles [10], etc.

The first distribution recovery in heterogeneous reactions was proposed more than 60 years ago and made by the approximate replacement of exponentials by the Heaviside functions [1]. This estimation with some modifications is still being used [11]. However, it is useless for distributions with a certain shape (for example, narrow) and does not correspond to the accuracy of modern experiments. Several more precise methods have by now been developed to determine distributions as applied to fluorescence studies, where the kinetic curve of fluorescence decay is complicated by convolution with an excitation pulse and cannot be obtained without knowing the lifetime distribution [12]. These methods were compared in [13–15]. However, no method is available for the recovery of distributions that provide an exact description of the kinetics of chemical reactions. A distribution can be recovered only for some simple kinetic functions, such as that in the geminal recombination of electron-cationic pairs [3]. When the experimental conditions change, the kinetics of the same reaction becomes more complicated, and the distribution cannot be recovered [3].

The problem of the distribution recovery is also complicated by a possible ambiguous solution of the inverse problem, which is observed sometimes for kinetic curves distorted by convolution [16]. The uniqueness of the solution is assumed to be achieved with quite a high accuracy of both experiment and its description [15, 17, 18].

In this work, a method for distribution recovery in chemical reactions of a first order is proposed. The solutions of the inverse problem were obtained by this method. This allowed us to analyze their properties and to propose unambiguous characteristics of reactivity in terms of statistical invariants of distributions.

METHOD FOR DISTRIBUTION RECOVERY

For a discrete set of n states, the kinetic curve of a reaction can be represented as the sum

$$Y(t) = \sum_{i=1}^{n} a_i \exp(-k_i t), \tag{1}$$

where $Y(t)$ is the concentration (or a quantity proportional to the concentration) at the moment t, and a_i and k_i are the amplitude (concentration) and rate constant of the ith state, respectively.

For a continuous set of states, the sum in Eq. (1) is replaced by the integral

$$Y(t) = \int_0^\infty a(k)\exp(-kt)dk, \qquad (2)$$

where $a(k)$ is the distribution density over rate constants k.

To find the discrete distribution corresponding to experimental data $Y_j(t_j)$, one has to solve the set of Eqs. (3) with respect to the unknown quantities a_i and k_i

$$\sum_{i=1}^{n} a_i B_{ij} = Y_j, \quad j = 1, 2, \ldots, N, \qquad (3)$$

where $B_{ij} = \exp(-k_i t_j)$ and N is the number of experimental points and the corresponding equations.

The set of Eqs. (3) can be solved by iterative methods and has a variety of approximate solutions because of the inevitable error in experimental data. Since this problem is classified as incorrect according to Tikhonov, a search for a stable solution is performed under the conditions of various types [12, 16]. The requirement that the number of particles $a_i \geq 0$ be nonnegative already eliminates solutions without physical meaning [10]. The best solution is selected from the remaining solutions under the condition that the calculated curve $Y(t)$ has a minimal deviation from the experimental points according to the χ^2 criterion:

$$\chi^2 = \frac{1}{N-p}\sum_j \left[\frac{Y(t_j) - Y_j}{\sigma_j}\right]^2 = 1 \pm 0.1, \qquad (4)$$

where p is the number of unknown quantities and σ_j is the error of the jth measurement. The calculated $Y(t)$ curve is strictly contained in the set of data points under the condition that $\chi^2 = 1 \pm 0.1$.

For the recovery of a continuous distribution, one can apply the same approach as in the exponential series method (ESM) [14] for the deconvolution of the fluorescence decay curve. According to ESM, the integral in Eq. (2) is replaced by the approximate sum of many exponentials with fixed rate constants k_i, which are uniformly distributed in a prespecified interval on the logarithmic scale of k. As a result, the problem is reduced to the solution of the set of Eqs. (3) with constant coefficients B_{ij} with respect to unknown quantities a_i. The distribution recovered by ESM in the $a(\log k) - \log k$ plot consists of steps with equal widths, which approximately describe the true continuous distribution.

The above methods to be applied need *a priori* knowledge about the type (continuous or discrete) of the desired distribution. However, when studying the kinetics of chemical processes, the number of reactive states is usually unknown beforehand.

In this work, we developed a general and more accurate method of approximate solution recovery for the set of Eqs. (3). We may call it the method of hyperbolic series (MHS). It does not require the number of participants of the process to be known beforehand. For distribution recovery using MHS, let us assume that all reactive states can be divided into n groups, each of which contains different states in such a way that the number of states in the ith group decreases in the course of the reaction according to the law $c_i(1 + k_i t/\nu)^{-\nu}$, where c_i and k_i are the initial number of states and the kinetic parameter of the reaction in the ith group, respectively. In this case, the kinetic curve of the reactions can be represented as the sum of power functions of the hyperbolic type

$$Y(t) = \sum_{i=1}^{n} c_i\left(1 + \frac{k_i t}{\nu}\right)^{-\nu}, \qquad (5)$$

where n and ν are prespecified positive integers.

The $Y(t)$ function specified by Eq. (5) is an approximation and describes the reaction kinetics in a finite time interval, which is always implemented in the experiments. The function is convenient because it coincides with the exponential function in any finite interval of variation of the argument $0 \leq x \leq x_{\max}$, so that the $(1 + x/\nu)^{-\nu}/\exp(-x)$ ratio differs from 1 by less than an indefinitely small value of $\varepsilon > 0$ at $\nu > (x_{\max})^2/2\varepsilon$.

The inverse Laplace transform of the $Y(t)$ function specified by Eq. (5) gives rise to the exact analytical expression for $a(k)$:

$$a(k) = \frac{\nu^\nu}{(\nu-1)!}\sum_{i=1}^{n} c_i k_i^{-\nu} k^{\nu-1} \exp(-k\nu/k_i). \qquad (6)$$

In order to seek $Y(t)$, we prespecified n, ν, the interval of possible k_i values, and the k_i values uniformly distributed in the specified interval on the logarithmic k scale. Then only the c_i parameters remain unknown. They are found from the set of Eqs. (3a) with the constant coefficients $H_{ij} = (1 + k_i t_j/\nu)^{-\nu}$ on condition that $c_i \geq 0$:

$$\sum_{i=1}^{n} c_i H_{ij} = Y_j, \quad j = 1, 2, \ldots, N. \qquad (3a)$$

The number of groups n can be assumed to be quite high. We took $n = 10$–100. If some groups turn out to be unnecessary, c_i corresponding to these groups are found to be equal to 0. Therefore, the approximating function $Y(t)$ can be very complicated with many fitting parameters c_i. This provides broad possibilities for a search for the most exact description of the kinetic curve. As soon as it has been found, the corresponding distribution is automatically obtained from Eq. (6). Since at $\nu \longrightarrow \infty$ Eq. (5) is transformed into Eq. (1), the MHS

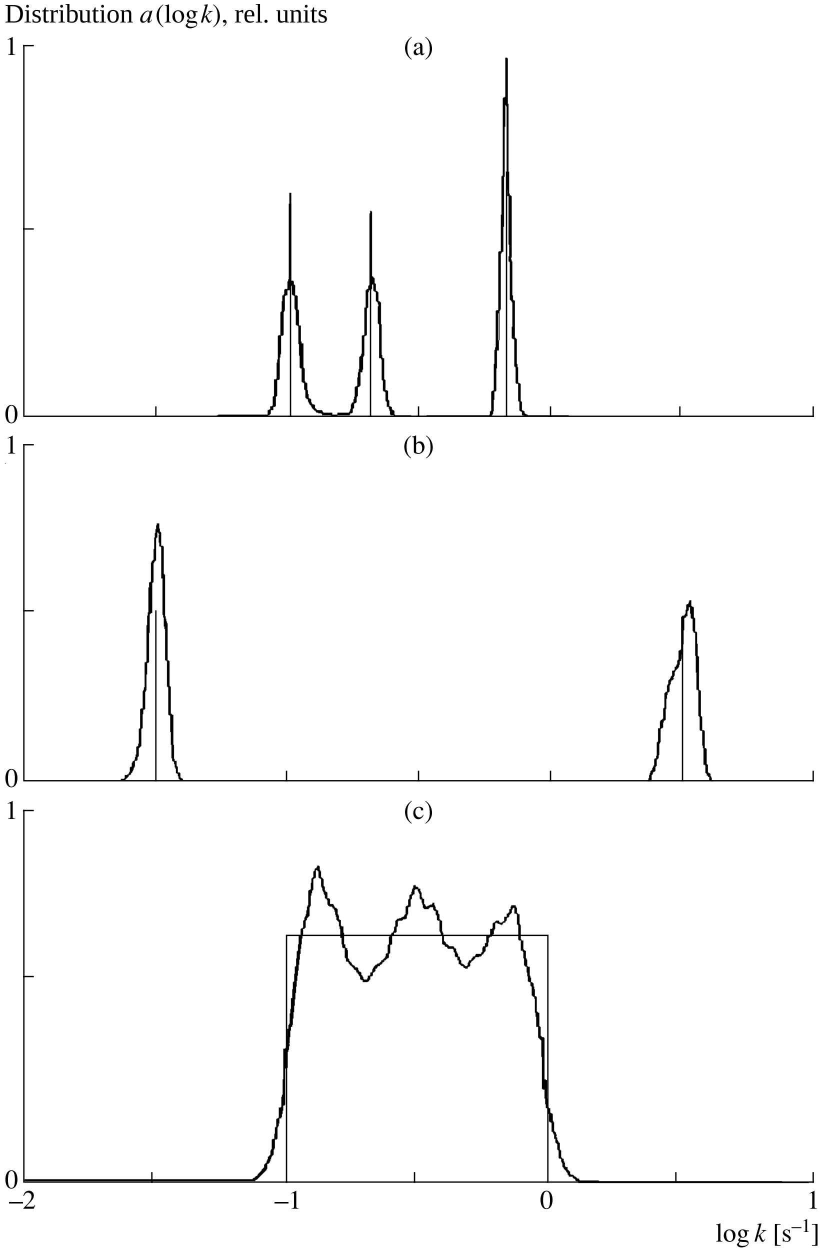

Fig. 1. Recovery of distributions using the method of hyperbolic series: (a) 3 : 3 : 4 ternary system, (b) 1 : 1 binary set; (c) rectangular continuous distribution. True distributions are shown by vertical lines.

can be used to determine both continuous and discrete distributions.

To check the MHS, we simulated the kinetic curve of a first-order reaction with specified distributions for cases when the data scatter is described by the Gaussian or Poisson statistics. The exact kinetic curve $Y(t)$ specified by the true distribution was calculated using Eq. (1) when $Y(t)$ changed from 10^6 to 2×10^3. The experimental values of Y_j at the moment t_j (number of points $N = 500$) were obtained as the Poisson or Gaussian random value with a mean equal to the exact $Y(t_j)$ value. Then the inverse problem was solved: the MHS was used to search for the $a(k)$ distribution, which describes experimental data.

Figure 1 shows that the proposed method can recover an unambiguous solution, distinguish a continuous distribution from a discrete one, and determine the number of active reaction centers. For example, the MHS finds the valid distribution for a 3 : 3 : 4 ternary system (Fig. 1a), and the acceptable value $\chi^2 = 1.075$ is achieved at $\nu = 1000$. This distribution is formally continuous. However, the parameters found are grouped in three narrow k intervals so that the distribution obtained can be considered to be discrete. A further increase in

$\nu > 1000$ results only in a narrowing of the found peaks, and at lower $\nu < 1000$ none of the other distributions agrees with the experiment. Similarly, for a 1 : 1 binary system, the MHS finds a valid discrete distribution with the same composition (surface areas under the peaks are the same) (Fig. 1b), and the acceptable value $\chi^2 = 1.12$ is achieved at values as low as $\nu = 200$. For a system with a continuous distribution of states, the MHS finds a distribution that is close to true and provides a valid description of the kinetics ($\chi^2 = 1.06$) already at $\nu = 150$ (Fig. 1c).

Thus, the MHS gives inverse problem solutions describing experimental data with the highest accuracy restricted by the experimental error.

Although the results obtained show that an unambiguous solution of the inverse problem using MHS is really possible, strictly speaking, many examples of unambiguous solutions do not prove its uniqueness for any sets of states. On the other hand, one example is sufficient to prove that ambiguity is possible. Using the MHS, we found that some quite complicated distributions that differ considerably in shape give kinetic functions coinciding in an interval of concentrations that varies by 18 orders of magnitude. In order that the difference in these functions exceed 1%, a change in concentration of 24–30 orders of magnitude is required, which is higher than reasonable experimental possibilities. This situation forced us to give special attention to an analysis of ambiguous solutions.

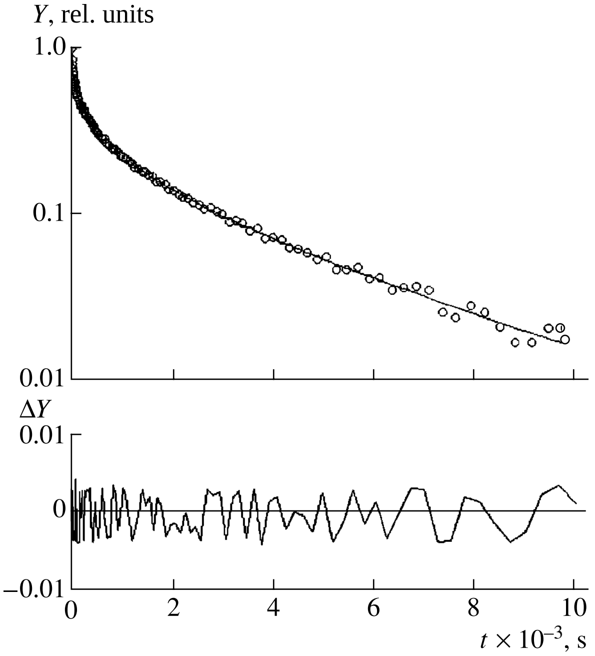

Fig. 2. (a) Kinetic curves of the first-order reaction involving 10 reactive states with the specified composition (set A, $a_i = 0.1$, $k_i = 2^i \times 10^{-4}$) (solid line) and experimental points ($N = 100$) with the scatter according to the Gaussian statistics; (b) deviations ΔY of experimental points from mean values.

AMBIGUOUS SOLUTIONS OF THE INVERSE PROBLEM

For a search and analysis of ambiguous solutions, we simulated the kinetic curves of a first-order reaction with the specified discrete set A of 10 reactive states with equimolar composition.

The exact kinetic curve $Y(t)$ specified by set A (solid line) and experimental points (their number was taken as equal to $N = 100$) with the random scatter according to the Gaussian statistics with the mean-square error of measurements $\sigma_{\mathrm{exp}} = 0.003$ are presented in Fig. 2a. The deviations of the experimental points from the exact curve $\Delta Y_j = Y_j - Y(t_j)$ characterizing the scatter of experimental data are presented in Fig. 2b.

The subsequent solving of the inverse problem by the standard search for a discrete distribution of several states recovers a series of discrete sets describing the same kinetic curve $Y(t)$ with approximately the same mean-square error σ equal to the experimental error σ_{exp}. Some of the recovered distributions, in addition to the true distribution A of 10 states, are presented in Fig. 3: set B of 16 states, C of 7 states, and D of 3 states. The same data can easily be described by sets with a higher number of states. Since all these distributions give the equivalent description of the experiment, we can conclude that a variety of discrete solutions to the problem exist, and the desired number of reactive states for sufficiently complicated sets is, thus, uncertain.

Some continuous distributions recovered by MHS are presented in Fig. 4. To verify the accuracy of the solutions, the kinetic curve of the reaction was calculated from the recovered distributions by applying Eq. (5), and then this curve was compared with the experimental data. At $\nu > 3$ the error σ of kinetics description by the recovered distributions is found to be the same and equal to the experimental error ($\sigma = 0.003$). Note that the deviations (ΔY) of the experimental data from the calculated curves shown in Figs. 4 and 2 almost coincide. This means that the method proposed provides the highest accuracy of solutions and finds the optimal fitting curve, which virtually coincides with the true curve of the reaction at the absolute accuracy of measurements. Thus, neither the accuracy of measurements nor the accuracy of analysis can be a criterion for the choice of the true distribution from a variety of solutions.

To confirm this conclusion, simulation experiments were performed with the highest (possible to date) accuracy of measurements. The number of experimental points with the random scatter according to the Poisson statistics was taken as equal to $N = 500$. The initial signal was taken as equal to $Y(0) = 10^6$. Under these conditions, the initial error of measurements is 0.1%. The examples of continuous solutions recovered are

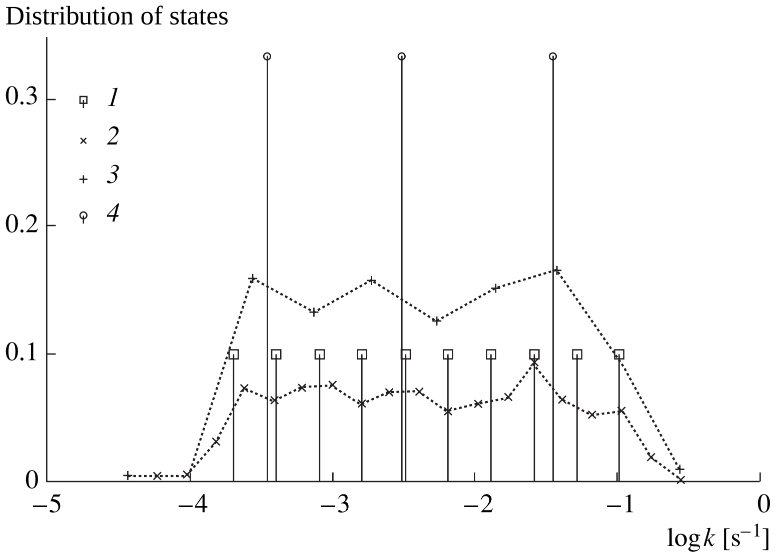

Fig. 3. Discrete distributions describing the kinetic curve in Fig. 2: (*1*) initial distribution A of 10 states and (*2*) recovered distributions B of 16 states, (*3*) C of 7 states, and (*4*) D of 3 states. Amplitudes for B and C are marked by dotted lines for clarity.

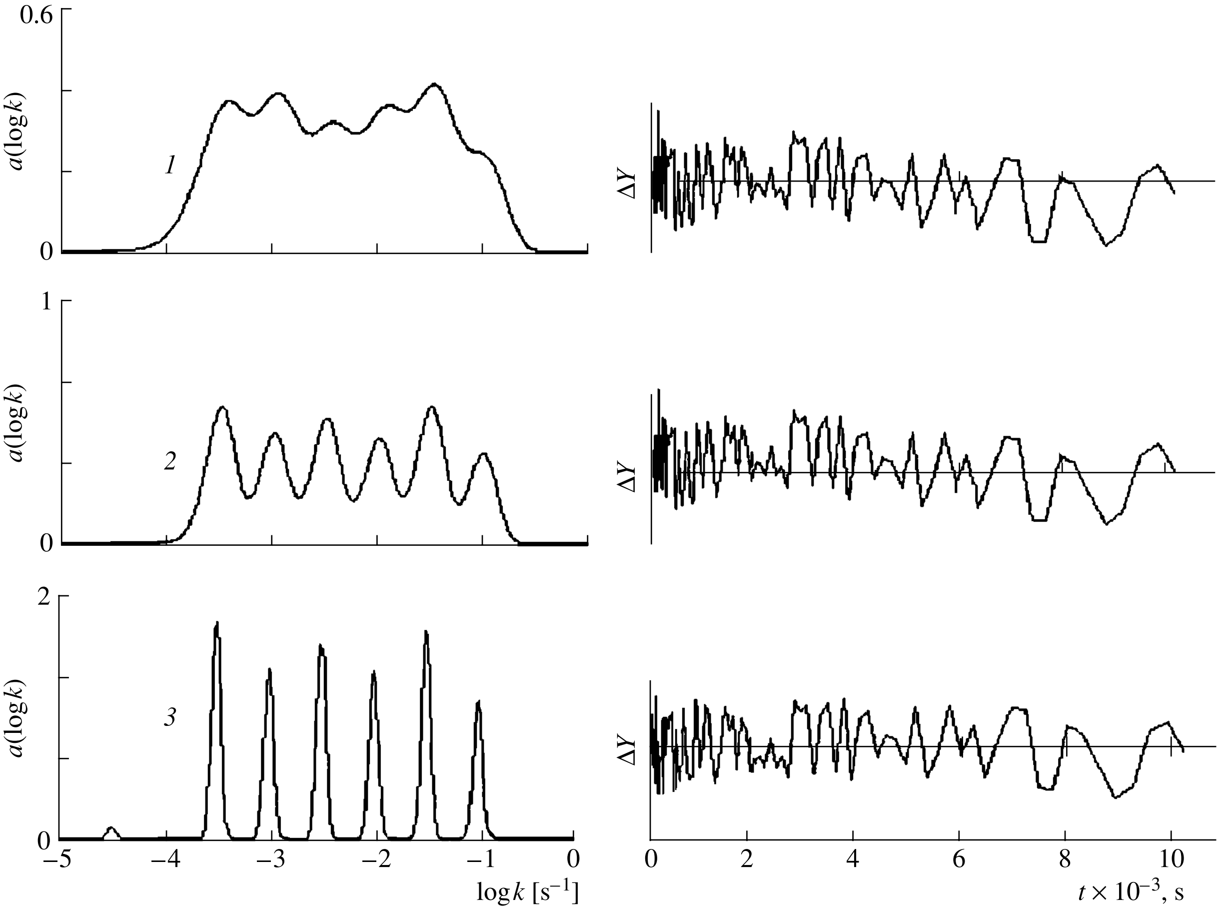

Fig. 4. Continuous distributions describing the experimental data presented in Fig. 2 and curves approximating them by Eq. (5) at $n = 20$ and parameter ν equal to (*1*) 4 (distribution E), (*2*) 10 (distribution F), and (*3*) 100 (distribution G). The corresponding deviations Δ*Y* of the experimental points from the calculated curves are presented on the right.

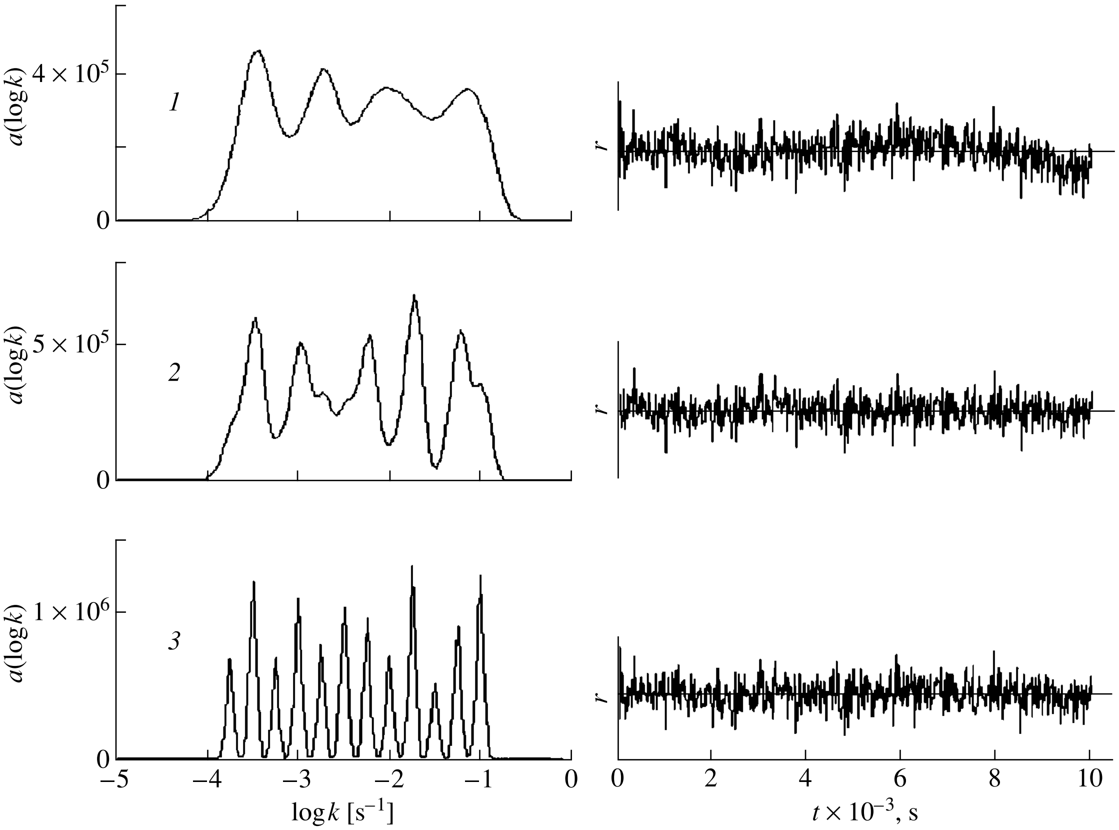

Fig. 5. Continuous solutions $a(k)$ of the inverse problem for the reaction specified by set A (Poisson statistics, number of experimental points $N = 500$) found by the MHS at $n = 20$ and parameter n equal to (*1*) 6 (distribution P1), (*2*) 20 (distribution P2), and (*3*) 150 (distribution P3) and residuals r of the experimental points from the fitting curves.

presented in Fig. 5. Residuals r (as the characteristics of differences between the experimental points and the kinetic curves computed from the recovered distributions) were calculated using the equation

$$r_j = [Y_j - Y(t_j)]/\sigma_j. \quad (7)$$

As follows from Fig. 5, despite the highest accuracy of the model experiment, there is a variety of distributions describing the experimental data with approximately the same residual profile. Moreover, the accuracy of the fitting does not allow us to draw a conclusion about the shape of the true distribution. For example, distribution P3 (at $\nu = 150$) is closer to a discrete one than distribution P2 (at $\nu = 20$) but gives a somewhat higher ($\chi^2 = 1.09$) error of the fitting compared to that for P2 ($\chi^2 = 1.08$).

The results obtained show that the solution of the inverse problem for a multicomponent reaction of the first order can be uncertain. In such cases, to choose the valid solution, the exact number of participants of the process should be determined in additional experiments.

Uncertainty is usually avoided using the so-called principle of lowest expenses: the simplest solution, which requires the lowest number of parameters, is preferable [16]. For example, discrete distributions of two to three states are usually used for the description of fluorescence decay [12, 19]. However, this approach does not guarantee that the chosen distribution is true. As a result, characteristics of states that probably do not exist, are obtained.

INVARIANTS OF SOLUTIONS OF THE INVERSE PROBLEM

The obtained solutions have common properties: distributions different in shape lie in approximately the same interval of the k values as the true distribution does; in addition, they reproduce the kinetic curve of the reaction. Therefore, we can assume that a set of inverse problem solutions has invariants, that is, quantities retaining their values on going from one distribution to another. To check this assumption, we chose the initial moments of normalized distributions of the sth order as possible invariants:

$$\overline{k^s} = \int_0^\infty k^s a(k) \mathrm{d}k = \sum_{i=1}^{n} k_i^s a_i, \quad (8)$$

$$\overline{(\ln k)^s} = \int_0^\infty (\ln k)^s a(k)\mathrm{d}k = \sum_{i=1}^{n} (\ln k_i)^s a_i. \quad (9)$$

The results of calculation of the moments of the recovered distributions are presented in Tables 1 and 2. The same results were obtained with different realizations of experimental data. It can be seen that $\overline{1/k}$, $\overline{\ln k}$, and $\bar{k}$ change slightly (within 10%) on going from one distribution to another. Their values are close to the true moments of distribution A. This is valid even when the error of kinetics description by the found solution is two times higher than the experimental error (Table 1, distribution D with $\sigma = 0.006$).

The accuracy of determination of the moment decreases with an increase in its order s. Nevertheless, the scatter of $\overline{k^2} = 0.0014$–0.0019 s^{-2} and $\overline{k^3} = (1.2$–$3.0) \times 10^{-4}$ s^{-3} remains appropriate for an unambiguous characterization of the distributions describing the kinetics with an error no higher than the experimental error. It is important that enhancing the accuracy of measurements (Table 2) enables one to decrease the scatter of the $\overline{k^2}$ and $\overline{k^3}$ values. In this case, the distributions, which correctly describe the kinetics (that is, for which $\chi^2 = 1 \pm 0.1$), give moment values that almost coincide with the true moments despite the ambiguity of the distributions themselves.

Thus, the moments of distributions from a set of inverse problem solutions are approximately invariants, whose accuracy of determination results from the experimental error and the accuracy of kinetics description. The moments are invariant because they are unambiguously related to the reaction kinetics. At $s = -1$, it follows from Eq. (8) that

$$\overline{1/k} = \int_0^\infty Y(t)\mathrm{d}t. \quad (10)$$

One can easily be convinced of the latter by inserting the expressions for $Y(t)$ by Eqs. (1) or (2) into Eq. (10). Thus, the mean value of $\overline{1/k}$ is equal to the area under the kinetic curve $Y(t)$ and, hence, is an invariant of distributions describing this curve. Since low $1/k$ make the largest contribution to the sum of inverse k values, the quantity

$$k_{\mathrm{low}} = 1/(\overline{1/k}) \quad (11)$$

is a statistical characteristic of reaction rate constants for the states with low reactivity.

Table 1. Moments of normalized distributions found for the model kinetic curve of the reaction specified by distribution A (100 points, Gaussian statistics, $\sigma_{\mathrm{exp}} = 0.003$)

Distribution*	σ	$\overline{1/k}$, s	$\overline{\ln k}$	$\bar{k}$, s^{-1}	$\overline{k^2} \times 10^3$, s^{-2}	$\overline{k^3} \times 10^4$, s^{-3}
A	0.003	999	–5.39	0.020	1.4	1.2
B	0.003	1030	–5.39	0.021	1.7	2.1
C	0.003	1060	–5.39	0.022	1.9	3.0
D	0.006	946	–5.47	0.014	0.5	0.2
E	0.003	1058	–5.38	0.022	1.9	2.6
F	0.003	943	–5.39	0.021	1.6	1.8
G	0.003	1160	–5.40	0.021	1.5	1.3

* The distributions are presented in Figs. 3 and 4.

Table 2. Moments of normalized distributions found for the model kinetic curve of the reaction specified by distribution A (500 points, Poisson statistics, $Y(0) = 10^6$)

Distribution*	χ^2	$\overline{1/k}$, s	$\overline{\ln k}$	$\bar{k}$, s^{-1}	$\overline{k^2} \times 10^3$, s^{-2}	$\overline{k^3} \times 10^4$, s^{-3}
A	1.04	999	–5.39	0.020	1.4	1.2
P1	1.33	1014	–5.30	0.022	1.8	2.1
P2	1.08	1007	–5.38	0.020	1.4	1.3
P3	1.09	1001	–5.38	0.021	1.5	1.3

* The distributions are presented in Figs. 3 and 5 (without normalization).

At $s = 1$, we obtain from Eqs. (1), (2), and (8) that

$$\bar{k} = \left.\frac{\mathrm{d}Y(t)}{\mathrm{d}t}\right|_{t=0}. \qquad (12)$$

Equation (12) suggests that the mean value of the rate constant $\bar{k}$ is equal to the initial reaction rate for all distributions describing the kinetic curve $Y(t)$ and, hence, is an invariant of these distributions. Since the high k values contribute greatly to the sum of the k values, the quantity

$$k_{\mathrm{high}} = \bar{k}$$

is a statistical characteristic of reaction rate constants for the states with high reactivity.

Similarly, at $s > 1$ the expressions for the sth derivative at zero time can be obtained from Eqs. (1), (2), and (8):

$$\overline{k^s} = \left.\frac{\mathrm{d}^sY(t)}{\mathrm{d}t^s}\right|_{t=0}. \qquad (13)$$

The mean values of k^s are also invariants. However, the accuracy of their determination decreases with an increase in s. As is well known, the numerical differentiation of the functions can be applied up to $s < 5$.

The mean value of $\ln k$ is related to the reaction kinetics by the more complicated relation

$$\overline{\ln k} = -\int_0^\infty \frac{Y(t) - \exp(-t)}{t}\mathrm{d}t. \qquad (14)$$

To prove Eq. (14), one has to replace the lower limit of integration of its right part by the low ε value, insert the expression for $Y(t)$ from Eqs. (1) or (2), integrate with respect to t, and go to the limit at $\varepsilon \longrightarrow 0$.

As follows from Eq. (14), the value of $\overline{\ln k}$ is an invariant of the solutions describing $Y(t)$. It determines the center of gravity of the distribution on the logarithmic scale of k and halves the area under the symmetrical distribution. The value of k_{w} at the center of gravity of the distribution can be found from the equation

$$k_{\mathrm{w}} = \exp(\overline{\ln k}). \qquad (15)$$

It is a statistical characteristic of the medium interval of reaction rate constants. It can be named the weight-average rate constant and has a significant distinctive feature: regardless of the distribution shape, the concentration decreases by a factor of about e at the time $\tau_{\mathrm{w}} = 1/k_{\mathrm{w}}$.

The expressions relating the reaction kinetics to the moments of a higher order of $s > 1$ can be obtained similarly. However, already the first three invariants (k_{high}, k_{w}, and k_{low}) determined from the initial rate, the center of gravity of the distribution, and the area under the kinetic curve give sufficiently important characteristics of the true distribution. The distance between k_{high} and k_{low} on the logarithmic scale of k quantitatively characterizes the distribution width, and their positions relatively to the weight-average constant at the center of gravity suggest a degree of asymmetry of the distribution. In symmetrical distributions, $\ln k_{\mathrm{w}}$ lies in the middle between $\ln k_{\mathrm{low}}$ and $\ln k_{\mathrm{high}}$. In asymmetrical distributions, if, for example, $\ln k_{\mathrm{low}}$ is farther from the center of gravity than $\ln k_{\mathrm{high}}$, the left descending region of the $a(\ln k)$ curve with low rate constants is more elongate.

Note that the calculation of invariants can also be applied to both broad and very narrow distributions. For a monoexponential kinetic curve, all of the three invariants (k_{high}, k_{w}, and k_{low}) coincide and equal the true rate constant. In this case, they are merely different determinations of the same rate constant. Therefore, their exact coincidence is a criterion for a simple reaction of the first order.

APPLICATION OF INVARIANTS

The kinetics is ambiguously described, for example, in analysis of the fluorescence decay of Rhodamine 6G in porous SiO_2 glass [20]. Thus, Hungerford *et al.* [20] found that with a dye concentration of 0.24 mM the reactivity of the dye can be explained by two mutually exclusive sets of states. The short-lived state predominates in the first set ($a_1 = 0.72$, $\tau_1 = 3.37$; $a_2 = 0.28$, $\tau_2 = 4.66$). The long-lived state prevails in the second set ($a_1 = 0.47$, $\tau_1 = 3.10$, $a_2 = 0.53$, $\tau_2 = 4.30$). None of the found sets can be preferred because both of them contain a minimal number of parameters and describe the experimental data with the same accuracy. This uncertainty can be eliminated using invariants. Inserting the values of a_i and $k_i = 1/\tau_i$ into Eqs. (8) and (9), one can easily be convinced that the invariants of Rhodamine 6G fluorescence retain their values on going from one set to another. For example, both sets give the same value $\tau_{\mathrm{w}} = 3.7$ ns ($\ln\tau_{\mathrm{w}} = 0.72\ln 3.37 + 0.28\ln 4.66 = 0.47\ln 3.10 + 0.53\ln 4.30$). Thus, despite an uncertainty in the inverse problem solution, the unambiguous characteristics of Rhodamine fluorescence was obtained.

Let us consider published data [4] on the fluorescence decay of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (PFP) in the Langmuir–Blodgett layers as the second example of the application of invariants. The kinetics of this process is multiexponential and described by discrete distributions. With an increase in the PFP concentration, the distributions (due to their uncertainty) change irregularly. Thus, the concentration dependence of the reaction kinetics cannot be judged. Using the data on the distributions (Table 1 in [4]), we calculated the invariants of the fluorescence decay of PFP. The results of the calculation (Fig. 6) show that the fluorescence of PFP is characterized by a narrow symmetrical distribution, whose width decreases with PFP concentration. The k_{low}, k_{w}, and k_{high} invariants systematically decrease with PFP concentration, indicating an interesting phenomenon: the slowing down of fluorescence decay. In fact, this phenomenon is seen in the kinetic curves without analysis. However, the phenomenon can be quantitatively characterized by the calculation

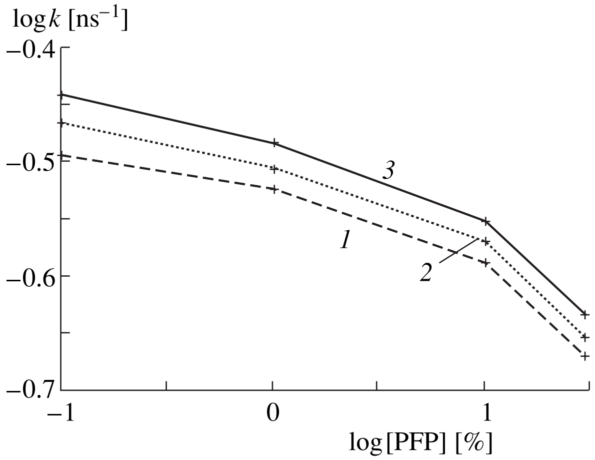

Fig. 6. Plot of the invariants (*1*) k_{low}, (*2*) k_{w}, and (*3*) k_{high} of PFP fluorescence decay in the Langmuir–Blodgett layers vs. PFP concentration (calculated from the published data [4]).

of invariants. As can be seen in Fig. 6, the region of high concentrations is of greatest interest, where the invariants decrease especially strongly, so that further change in the structure of the PFP aggregates could result in a more considerable slowing down of fluorescence decay.

CONCLUSION

In this work, the method of hyperbolic series was proposed for the determination of distributions in first-order chemical reactions. The method was verified for model systems to demonstrate that it recovers the distribution corresponding to experimental data with the highest accuracy. It does not require any *a priori* knowledge of the type of the initial distribution, and it can be applied to a search for both continuous and discrete distributions.

Using this method, we found that distributions with different shapes can give the same reaction kinetics coinciding to very high degrees of conversion. Hence, an ambiguity of distributions is a property inherent in the kinetic description of a multicomponent system.

Under conditions of uncertainty, we propose the use of invariants determined from the moments of distributions. The approach based on invariants is advantageous compared to the traditional analysis of distributions. First, the invariants do not require *a priori* hypotheses and seriously restrict arbitrariness in the interpretation of kinetic data. Second, they provide unambiguous quantitative characteristics of the true distribution. Third, the invariants make it possible to monitor the experimental accuracy necessary for reliable estimations. For example, if an invariant does not retain its value on going from one of the found distributions to another, in order to estimate it reliably the accuracy of measurements needs to be increased. Finally, the more invariants are determined, the more complete is the information on the true distribution. As is known from statistical physics, the knowledge of all moments is equivalent to the knowledge of the distribution.

Note that the use of invariants provides unambiguous quantitative characteristics of the reactivity of compounds in multicomponent reactions.

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REFERENCES

1. Roginskii, S.Z., *Geterogennyi kataliz* (Heterogeneous Catalysis), Moscow: Nauka, 1979, p. 416.
2. Emanuel', N.M. and Buchachenko, A.L., *Khimicheskaya fizika molekulyarnogo razrusheniya i stabilizatsii polimerov* (Chemical Physics of Molecular Degradation and Stabilization of Polymers), Moscow: Nauka, 1988, p. 368.
3. Bagdasar'yan, Kh.S., *Kinetika rekombinatsii v zhidkoi srede* (Kinetics of Recombination in Liquid Medium), Moscow: Nauka, 1989, p. 96.
4. Efimov, A.V., Anikin, M., Tkachenko, N.V., *et al.*, *Chem. Phys. Lett.*, 1998, vol. 289, p. 572.
5. Barra, M. and Scaiano, J.C., *Photochem. Photobiol.*, 1995, vol. 62, no. 1, p. 60.
6. Egelhaaf, H.-J., Lehr, B., Hof, M., *et al.*, *J. Fluorescence.*, 2000, vol. 10, no. 4, p. 383.
7. Enescu, M. and Lindqvist, L., *Photochem. Photobiol.*, 1995, vol. 62, no. 1, p. 55.
8. Whitten, D.G., Farahat, M.S., and Gaillard, E.R., *Photochem. Photobiol.*, 1997, vol. 65, no. 1, p. 23.
9. Siemiearczuk, A., Ware, W.R., and Liu, Y.S., *J. Phys. Chem.*, 1993, vol. 97, p. 8082.
10. Gakamsky, D.M., Goldin, A.A., Petrov, E.P., *et al.*, *Biophys. Chem.*, 1992, vol. 44, p. 47.
11. Barashev, P.P., *Khim. Fiz.*, 2001, vol. 20, no. 2, p. 34.
12. Ghiggino, K.P., Roberts, A.J., and Phillips, D., *Adv. Polym. Sci.*, 1981, vol. 40, p. 69.
13. O'Connor, D.V., Ware, W.R., and Andre, J.C., *J. Phys. Chem.*, 1979, vol. 83, no. 10, p. 1333.
14. Siemiarczuk, A., Wagner, B.D., and Ware, W.R., *J. Phys. Chem.*, 1990, vol. 94, no. 4, p. 1661.
15. Novikov, E.G., *Opt. Commun.*, 1998, vol. 151, nos. 4–6, p. 313.
16. Liu, Y.S. and Ware, W.R., *J. Phys. Chem.*, 1993, vol. 97, no. 22, p. 5980.
17. Novikov, E.G., van Hoek, A., Visser, A.J.W.G., *et al.*, *Opt. Commun.*, 1999, vol. 166, no. 8, p. 189.
18. Sadlej-Sosnowska, N. and Siemiarczuk, A., *J. Photochem., Photobiol. A: Chem.*, 2001, vol. 138, no. 1. p. 35.
19. Hofstraat, J.W., Verhey, H.J., Verhoeven, J.W., *et al.*, *Polymer*, 1997, vol. 38, no. 12, p. 2899.
20. Hungerford, G., Suhling, K., and Ferreira, J.A., *J. Photochem., Photobiol. A: Chem.*, 1999, vol. 129, no. 12, p. 71.