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REGRESSION ANALYSIS OF ISOBAR BOILING POINT OF WATER-ORGANIC BINARY MIXTURES

© 2017 M. A. Preobrazhenskii, O. B. Rudakov, M. I. Popova

Voronezh State Technical University, 84 20-letija Oktjabrja str., 394006 Voronezh, Russia
e-mail: robi57@mail.ru

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Abstract. We developed an algorithm for separating the non-stochastic contribution to the empirical dependence of the physicochemical properties of binary solutions on the concentrations of the components. The algorithm is based on the different behaviours of stochastic and deterministic coefficients of Fourier expansions. It was proved that the isolation of a non-additive part of the dependence allows a quantitative description of the contribution of the solvating effects on the system's energy. In addition, this isolation is necessary for the analytical continuation of the studied function in the formalized area of negative values of concentrations. It was proved that the suggested development allows separating the stochastic part of the empirical data. We determined the qualitative criteria for the separation of deterministic and stochastic Fourier harmonics.

We suggested an efficient three-parameter basis for the regressive description of the isobar of the boiling points of binary solutions. It was proved that the first component of the basis already describes the greater part of non-stochastic empirical information. We formulated a two-stage algorithm for the regressive description of the isobar of the boiling point of aqueous-organic solutions. That algorithm can reduce the amount of necessary empirical information. We also calculated the regression model coefficients for a number of solutions with practical relevance. For most of the investigated solutions, one component of the three-parameter basis fully describes the empirical information. For less than 20% of the studied solutions, the regression basis needs to be supplemented with Fourier harmonics. The number of such harmonics does not exceed two. It was proved that the relative error of the proposed algorithm does not exceed 2% and can be explained by experimental errors.

Keywords: homogeneous mixture, water, organic solvents, isobar, the boiling point, Fourier expansion.

INTRODUCTION

The dependence of the composition properties of solutions has always attracted considerable interest, as determined by the role of these systems in engineering and applied chemistry. [1] This interest has generated a large and growing number of experimental studies on this [2, 3]. The foundation of modern ideas about the properties of solutions as thermodynamically equilibrium systems formed by individual components and their reaction products was laid by Mendeleev [4]. In the model of ideal solutions or infinitely dilute solutions [5], the physicochemical characteristics of the binary system $X(n)$ are bilinear functions of concentration *n* and the properties of the individual components X_1, X_2

$$X_a = X_1 n + X_2 (n-1) \qquad (1)$$

where molar concentrations of components $n \in [0,1]$. Physically, the approximation (1) neglects the effects of interaction of molecules of different components. However, the accuracy of this approximation is not sufficient for describing the properties of real systems in many cases. Thus, for a number of systems, the boiling point deviation from bilinear Raoul's law is fairly high in the extremum [6], which makes the task of developing methods of accounting for the effects of the interaction between component molecules in mixtures.

The modern theory describes the nonlinear effects in solutions by the mechanism of salvation, which covers different types of intermolecular interaction and leads to the disruption of the local (at the nanoscale) homogeneity of the system [7]. Despite considerable interest in the description of the solvation processes, there is no concept which is capable of explaining "ab initio" the observed phenomena and predicting new phenomena [8]. Numerous methods exist for the thermodynamic description of [9] and computer simulations [10, 11]. Even the simplest systems require knowledge of the chemical potentials of the interaction of particles, whose parameters are determined from empirical data. However, these methods provide only a qualitative description of the phenomena. Therefore, the practical methods for the quantitative description of real multicomponent systems do not use the model building stage, but are based on the direct regression approximation of empirical data [6, 12]. Error regression descriptions contain two components with fundamentally different minimization methods. Firstly, the experimental error is in most cases has a stochastic nature. Analyses of the causes of experimental errors in the measurement of physical and chemical characteristics of complex equilibrium systems has described in extensive literature (see ex, [12] and its references).

Significant dispersion of experimental results have been observed for a number of binary aqueous-organic solutions [6, 12, 13]. They show a notable stochastic contribution in empirical results. Not only the reduction, but the evaluation of experimental error, is a complex task. Therefore, there is a lack of evaluation of the reliability of experimental data in the most of the experimental studies of dependence of physicochemical characteristics of complex systems on its composition [6, 12, 13]. However, even the calculation of confidence intervals by statistical methods can only determine the lower boundary of integral contribution of stochastic processes [14]. Thus, this approach does not allow isolating deterministic and stochastic components experimental arrays and can be considered as only being diagnostic.

Errors which are related to the properties of the basis set of regression and the precision of the calculation method, have a fundamentally different behavior. These errors can be formally made arbitrarily small by expanding the basis set and optimization of numerical algorithms. In this case, the method of calculation of regression description errors depends on its purpose. The common purpose for the regression model of experimental data is interpolation or extrapolation. In this case, the standard methods of error estimation based on the correlation coefficient R (and related characteristics) are not sufficient to the task, because they get information from experimental points only. The interpolation errors are not controlled in this approach. For example, a Lagrange polynomial of degree $N-1$ exactly describes empirical array having N dimensions (formally whereby $R = 1$) [15] in the experimental points. However, a high degree polynomial demonstrates a sharp dependence on the argument between the experimental points even when the function is smooth. The situation is even worse in the presence of stochastic contribution, when significant errors are observed even in experimental points. The harmonic basis set or basis set of Chebyshev polynomials that is ideologically close to harmonic basis can be considered as adequate to this system. These basis sets allow minimizing the maximum error in all domain. However, practical application of regression basis sets with large variable number of parameters is undesirable.

In practice this can be used a closed basis set, which must satisfy two requirements. First, the parameters of regression basis set must provide a complete mapping of the non-stochastic part of the information. Second, the class of functions, where a basis set has been constructed, must describe the basic properties of the system. The symmetry properties, which represent the fundamental characteristics of systems, take a special place among all properties [17, 18]. The account of the symmetry properties in the regression basis set regardless of the completeness and accuracy of the array allows us to construct empirical description automatically reflected fundamental properties of the studied systems [19]. Thus, the wording of the symmetry properties and formation of invariant under these conversions basis set are compulsory steps for constructing regression descriptions adequate to this system.

Accounting for the properties of geometric symmetry (inversion, translational, rotational, chiral etc.) of individual molecules and permutation symmetry of atoms in molecule is widely used in chemistry [18, 20]. Additional symmetry, which is related to the transposition of characteristics and concentrations of individual components and which is then taken into account in the work [19], comes into existence in multicomponent systems. In particular, the basis of the regression must be invariant with respect to simultaneous interchange of the characteristics of the components and their concentrations.

The consideration of symmetry allows us to determine only a class of functions that form a basis set. The composition of the basis set can be determined by regression error, completeness, and accuracy of available empirical information. Consequently, the size of the optimum basis set has upper and lower boundaries. The upper boundary is determined by size of the basis, which provides a description of the non-stochastic part. The rise of basis set size over optimum size not only increases the amount of computation, but also brings stochastic component to the regression description. The lower boundary is determined from the conditions of complete mapping of deterministic information.

The purpose of this work is to develop methods for the isolation of stochastic component of empirical array and to optimize the parameters based on the regression basis set. The solution of this problem can be based on analysis of local behavior of empirical array or on analysis of entire set of input data as a whole [21]. The choice between these classes of algorithms is determined by the amount and analytical properties of empirical data. The main advantage of the local algorithm is that it is possible to use it for analyzing small arrays of empirical data. However, this class of algorithms is based on the assumption of local stationary of second derivative of approximated function in a locality of each used point. Therefore, as shown in [22], this algorithm is effective only in case of smooth functions, which significantly reduces the scope of its applicability. A local algorithm, in particular, is not applicable for arrays with large stochastic component with a non-analytic nature.

In this case, an alternative method for separating a smooth trend from stochastic changes, which is based on empirical analysis of the global array, will be adequate to the problem. The algorithm for separation examined dependence on deterministic and stochastic parts is based on the expansion of the function in a Fourier series [21]:

$$X(n) = \sum_{m=1}^{\infty} b_i \sin(\pi mn) + \sum_{m=0}^{\infty} c_i \cos(\pi mn). \qquad (2)$$

Here, unlike the equation (1), domain $n \in [-1,1]$ Therefore, the analytic continuation of the function X (n) to the formal area of negative values of n is necessary.

An analysis of the rate of convergence of the expansion (2) allows us to solve this problem. The proposed algorithm is based on the qualitatively different behavior of the Fourier expansion of dynamic and stochastic functions [21]. It allows not only evaluate, but also select non-stochastic part of empirical data. Various modifications of this algorithm are widely used in many fields of science and technology [23]. In case of presence sufficient empirical information, it allows to select deterministic part of the information even if the stochastic component has same power [24].

Calculation of M Fourier coefficients of the expansion of functions, which analytic representation is unknown (in particular – empirical functions), is possible only when set, at least, M values of functions [21]. Therefore, empirical information allows us to determine the finite number of harmonics of the expansion (2). Only some of those expansions describe a determined signal. The description of real systems by finite segment of (2) is justified only when convergence rate of the expansion is sufficiently rapid. Furthermore, finding of non-stochastic dependence on background of stochastic noise requires additional information. Therefore, effective use of currently available smoothing algorithms in case of growth of stochastic contribution requires an increase of the size of empirical arrays. However, the specific of physicochemical experiments does not allow satisfying this requirement with rare exceptions. Consequently, the development of algorithms for smoothing arrays of experimental data, which considers the specifics of the systems studied, is the aim of the present work. As an example of application of the proposed algorithm, description of dependence of the isobars of boiling temperatures of binary aqueous-organic solutions on concentrations has been considered. However, the range of applicability of this algorithm is much broader and includes descriptions of a wide class of physicochemical characteristics of homogeneous systems, which are in state of thermodynamic equilibrium.

EXPERIMENTAL

As it was shown in [25], the Fourier components (2) of continuous function, the first derivative of that function has discontinuity, decrease with the rate m^{-2}. However, if the function itself has discontinuities, the terms of the series do not decrease. The physical reason of the function discontinuities appearance is stochastic processes contribution to the observation results. There are some other discontinuity formation mechanisms, which are not related to the properties of the observation arrays. In particular, the function discontinuity may appear while its analytical extension to the formal area of negative concentrations values. The necessity of this appearance is determined by different definitional domains of the function $X(n)$ and its Fourier series. For the effective isolation of the determinate function component from the overlaid stochastic noise it is necessary to formulate an algorithm of analytical extension, which does not cause neither discontinuity of the function, nor its derivative. Isolation of the non-additive part of the dependency $X(n)$ allows us to solve the problem for a binary homogeneous solution:

$$\Delta X(n) = X(n) - [X_1(n) + X_2(1-n)]. \qquad (3)$$

Since the bilinear function (1) has permutable symmetry, invariant with respect to permutations of the characteristics of the components and concentrations, there also should be a non-additive amendment $\Delta X(n)$

Since the function $X(n)$ on the boarders of the definitional domain takes zero values, analytically it may be extended into the formal area $n \in [-1, 0)$ as a continuous odd function with continuous both first and second derivatives. Therefore, non-stochastic terms of the Fourier series decrease asymptotically at least as m^{-3} [25]. This rate of decrease makes the difference of behavior of non-stochastic and stochastic components very sharp. Such a rapid convergence of the Fourier expansion of non-stochastic part of the function $\Delta X(n)$ leads to the fact, that a small number of terms gives the main contribution to the non-stochastic part of the expansion:

$$\Delta X_{det}(n) = \sum_{m=1}^{M} b_m \sin(\pi mn). \tag{4}$$

Moreover, since the function $\Delta X(n)$ is an odd one, the terms of Fourier expansion which contain multipliers $\cos(\pi mn)$ are equal to zero. This effect causes an additional decrease in the necessary empirical information.

The coefficients of the sum (4) may be obtained directly from experimental data. Calculation of the coefficients b_m is reduced to the summation of a finite number of terms [21]. The most simple is the formula for calculation of coefficients b_m for equidistant experimental points on the interval [0, 1]:

$$b_m = \frac{2}{K}\sum_{k=1}^{K-1} \Delta X\left(\frac{k}{K}\right)\sin\left(\frac{k\pi m}{K}\right) \tag{5}$$

where K is the number of observation points and number of coefficients satisfies the condition $m \le K$. In the expression (5) is taken into account that due to the boundary conditions on the non-additive amendment $\Delta X(0) = \Delta X(1) = 0$, the sum (5) of terms with $k = 0$, K is equal to zero. If the experimental values obtained not at equidistant points, the required values of functions $\Delta X(k/K)$ can be obtained by interpolation in case of sufficient density and accuracy of the data.

As it was shown in [21], the partial section (4) of the Fourier series not only accurately describes the values of experimental points, but gives the least mean-squared error of interpolation in the whole domain for every single value of M. The error of this interpolation does not exceed the absolute value of the coefficient b_M at any point [16]. Analysis of convergence rate of the Fourier expansions of non-stochastic and stochastic components of the function $\Delta X(n)$ allows us to determine the number of non-stochastic harmonics M, relying only on the experimental data. Non-analytic behavior of random noises leads to appearance of higher harmonics in the Fourier expansion. Due to this fact, the sum (4), which describes the idealized case of absence of noises, is replaced by the expansion:

$$\Delta X(n) = \Delta X_{det}(n) + \sum_{m=M+1}^{\infty} b_m \sin(\pi mn). \tag{6}$$

For higher harmonics with $m > M$ almost uniform spectrum (the so-called white noise [29]) with infinite dispersion is observed. In the series (6) where $m > M$, a random signs alternation for b_m coefficients without their modulus reduction is observed. Amplitude of stochastic Fourier harmonics varies only due to fluctuations [27]. As an example, Figure 1 shows the dependence of the modules of expansion coefficient (6) of experimental results [6] on the harmonic number for the system "ethanol – water". The interval (m = 1–5), which has a rapid decrease in the amplitude of the harmonic as the number of harmonic increases, is obvious. In contrast to the non-stochastic term, for $m > 5$ modulus of coefficients b_m are not reduced, which indicates their stochastic nature.

The weak dependency of modules of stochastic Fourier coefficients on their numbers leads to the phenomenon when this part of the spectrum parameter χ, defined by the formula:

$$\chi_{jk} = \frac{1}{k}\sum_{m=M+j}^{M+j+k} b^2{}_m, \tag{7}$$

accurate within fluctuations, remains constant in case of varying lower limit of summation (j = 1, 2, …, $K - M - 1$), and the number of carried terms (k = 1, 2,…, $K - j - 1$). The contribution of fluctuations in the sum (7) reduces with an increasing number of terms k, which raise requires an increase of the number of observations K.

A quantitative measure of the stationary of parameter χ_{jk} is the relative dispersion

$$\varepsilon_M = \frac{1}{\bar{\chi}M}\sqrt{\sum_{j=1}^{K-M-1}\left(\bar{\chi}M - \chi_{j,K-j-1}\right)^2}, \tag{8}$$

where the average value $\bar{\chi}$ is determined by the equation

$$\bar{\chi}M = \frac{1}{K-M-1}\sum_{j=1}^{K-M-1}\chi_{j,K-j-1}. \tag{9}$$

The criterions for the separation of non-stochastic and stochastic harmonics are small values of dispersion (8) for all M.

All the harmonics with numbers exceeding the limit value M, have no non-stochastic information, but only show the presence of stochastic noise [26]. The rejection (smoothing) of those harmonics allows to

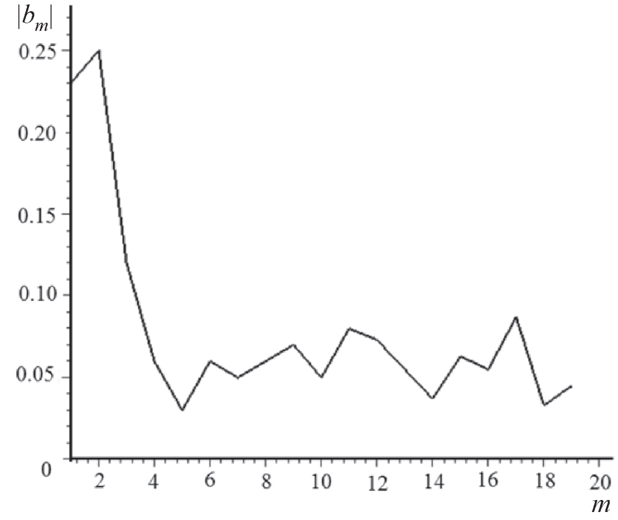

Fig. 1. The dependence of the modulus of the Fourier coefficients of the expansion (4) of non-additive amendment to boiling point isobar for the system “ethanol –water” $|b_m|$ on the harmonic number m

pick a real signal out of background noise. The number of experimental data points should be sufficient to describe deterministic signal and to analyze stationary of parameter χ_{jk}. If $K<M$, the amount of experimental data does not allow the investigated dependence $\Delta X(n)$ to be described, even with the absence of stochastic noise. The value $K = M$ defines the minimum set of statistical information, which is necessary to calculate a set of coefficients b_m, expressing the dependence $\Delta X_{\text{det}}(n)$ in the absence of noise. However, an ideal experiment cannot be practically implemented. Eventually, data smoothing is possible in case of $K > M$, however, due to fluctuations, it is efficient when $K \simeq 5M$. In reality, this number of experimental points is usually unavailable, which restricts the applications of this algorithm to the analysis of physicochemical systems. For example, as can be seen from Figure 1, the limit of stochastic overtones is determined by condition $M = 5$ and therefore, the number of experimental data for effective smoothing should be not less than the value $K \sim 25$–30. However, empirical arrays rarely meet this requirement [6, 12, 13]. Thereupon, the use of the algorithm for description of non-additive correction term, which is based on the expansion of function ΔX to a series (4), does not usually allow to identify the deterministic part of the empirical array and to smooth it effectively.

An algorithm for the smoothing of real experimental data cannot be universal, but it should be based on the consideration of the symmetry properties of the studied systems. As shown in [19], the isolation of the additive part (1) of empirical function not only allows us to avoid the discontinuities of the function and its derivatives, but also makes it possible to build a regression description, which considers the symmetry properties of a homogeneous system.

The regressive description algorithm of the determinate part of the information proposed in [19, 28] allows us to solve that problem. It is based on the consideration of symmetrical system properties, which provides an opportunity to isolate the stochastic contribution to empirical arrays, even with a lack of information. A modified algorithm is built up based on the description of the main determinate contribution ΔX, not a harmonic (4), but permutatively invariant function, defined by the described characteristic. Regression basis isotherms of density, dynamic viscosity, surface tension coefficient and refraction coefficient were obtained in [19]. A three-parameter basis set for description of boiling temperature isobars, which was obtained in [28], has the following form:

$$\Delta T_{inv} = \Delta T_e \cdot \sin\frac{\pi}{2}\left[\begin{array}{c}\dfrac{1-\exp(-\alpha n)}{1-\exp(-\alpha)}+\\ +\left[\dfrac{1}{2}+\dfrac{\arctan 10^3(n-n_e)}{\pi}\right]\dfrac{n-n_e}{1-n_e}\end{array}\right]. \qquad (10)$$

Algorithm for calculation of the parameters of permutative invariant regression ΔT_e, α и n_e has been formulated in previous study [28].

Fourier expansion (6) is constructed only for the difference $\delta T = \Delta T - \Delta T_{inv}$. Since the majority of the determinate information displayed by the function ΔT_{inv}, number of deterministic harmonics in the expansion of the difference δT is small and, according to the results of the calculations, the actual experimental arrays [6, 12, and 13] allow us to conduct an effective description and smoothing.

RESULTS AND DISCUSSION

The presented algorithm is implemented in the shell “Maple V Power Edition”. The calculation results of non-stochastic and stochastic contribution to the empirical dependences of boiling temperatures of some aqueous-organic solvents are given in the **table**. Boundary deterministic harmonic M is calculated from the condition $\varepsilon_M = 0.1$. Data in the table are arranged in order of decreasing of the number M and dispersion ε_M. The error of regression description for non-additive amendment can be described by a root-mean-square error, which can be defined as follow:

$$\sigma = \frac{1}{\sqrt{M(M-1)}}\sqrt{\sum_{i=1}^{M}\left(\Delta T_i^R - \Delta T_i^E\right)^2} \qquad (11)$$

Table. Calculation results of non-stochastic and stochastic contributions to empirical dependences of boiling temperatures of aqueous-organic solutions. M is the number of non-stochastic harmonics of expansion function δT; ε_M is dispersion of χ parameter; σ and σ_n are absolute and normalized to the maximum amendments of three-parameter approximation respectively; σ_f is normalized root-mean-square error of approximation with M non-stochastic harmonics

Organic solvent	M	ε_M	σ	σ_n	σ_f
Formic acid	2	0.089	0.133	0.0190	0.0094
Butanone	2	0.088	0.317	0.0138	0.0087
Isobutanol	2	0.063	1.103	0.0759	0.0231
1,4-Dioxane	1	0.082	0.739	0.0577	0.0211
Propionic acid	1	0.071	0.565	0.0195	0.0107
Allyl alcohol	1	0.065	0.254	0.0245	0.0057
Ethanol	0	0.097	0.064	0.0051	0.0051
1-Butanol	0	0.091	0.669	0.0424	0.0424
Furfurol	0	0.088	2.065	0.0423	0.0423
Methanol	0	0.083	0.031	0.0027	0.0027
Acetonitrile	0	0.077	0.038	0.0025	0.0025
Isopropanol	0	0.073	0.133	0.0087	0.0087
Cyclopentanol	0	0.071	0.621	0.0280	0.0280
Acetone	0	0.069	0.402	0.0170	0.0170
Butenone	0	0.067	0.330	0.0205	0.0205
Butyric acid	0	0.060	0.122	0.0035	0.0035
Ethylene glycol	0	0.057	0.087	0.0017	0.0017
1-Propapanol	0	0.055	0.386	0.0340	0.0340
Acetic acid	0	0.053	0.031	0.0062	0.0062
Dimethylformamide	0	0.049	0.176	0.0120	0.0120
Ethyl acetate	0	0.031	0.397	0.0140	0.0140

where ΔT_i^R and ΔT_i^E are regressive and experimental values of non-additive error respectively, n_i is the solvent concentration.

Absolute and normalized to the maximum amendments ΔT_e of root-mean-square errors of invariant approximation (10) (σ and σ_n, respectively) are shown. The last column shows the normalized root-mean-square error of approximation in case of consideration of non-stochastic terms of the Fourier expansion (11). Of course, in the absence of the Fourier expansion of the function of non-stochastic terms ($M = 0$) $\sigma_f = \sigma_n$.

CONCLUSION

According to the results of the calculations for most of the investigated water-organic solutions, the invariant approximation (11) completely describes the deterministic part of the empirical results. An example of dependence $\delta T_b(n)$, which only contains a stochastic component, is shown in Figure 2. For some systems, the approximation (10) does not fully describe the empirical data and can be refined by taking into account the non-stochastic harmonics of function δT_b, the value of which does not exceed two for all investigated solutions. Due to this fact, a very limited amount of empirical information allows us to construct an adequate description of the equilibrium binary systems. The accuracy of this description depends only on random experimental errors. An example of dependence $\delta T_b(n)$, which contains a non-stochastic component, is shown in Figure 3. The consideration of non-stochastic harmonics in the Fourier expansion of function $\delta T_b(n)$ allows us to reduce the relative error of the regression to values in 2–3 times, which does not exceed 2×10^{-2}. Further reduction of this error can only be achieved by reducing stochastic experimental errors.

In the presence of sufficient empirical information, the description of homogeneous solutions, based on the direct Fourier expansion of the non-additive part of dependence $T(n)$ or on the preliminary allocation of the approximation (10), are both possible. The second algorithm has demonstrated its efficiency in the presence of a sufficient amount of experimental data because it greatly reduces the amount of computation. It should be noted that the range of applicability of the proposed algorithm is much broader and includes the description of a wide class of physical and chemical properties of homogeneous systems in a state of thermodynamic equilibrium.

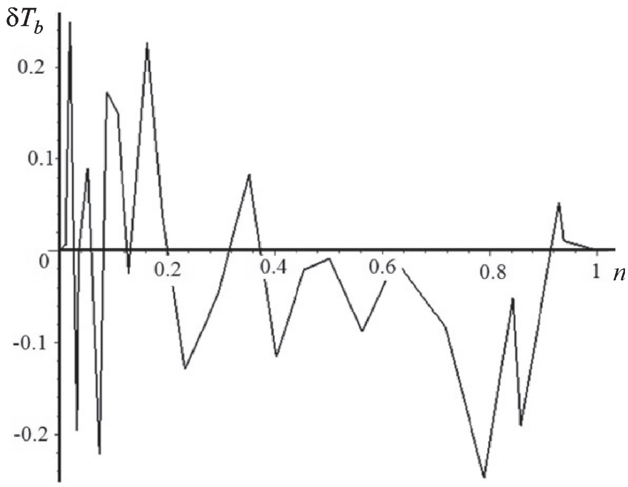

Fig. 2. Dependence of the difference $\delta T_b = \Delta T_b(n) - \Delta T_{inv}$ on concentration of methanol in a "methanol-water" mixture. This dependence does not include a non-stochastic component

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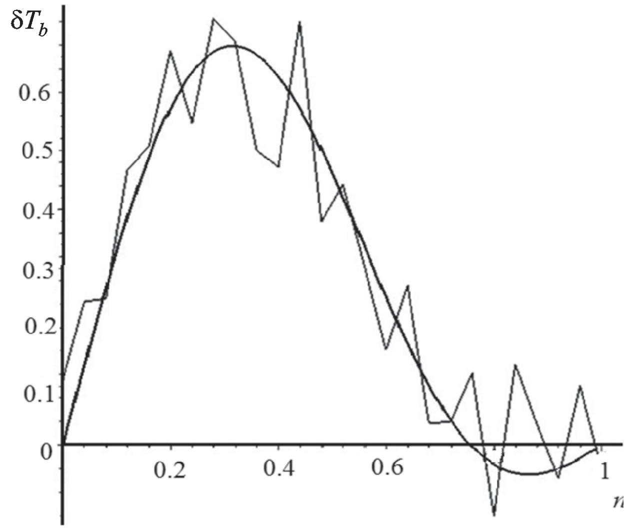

Fig. 3. Dependence of the difference $\delta T_b = \Delta T_b(n) - \Delta T_{\mathrm{inv}}$ on the concentration of isobutanol in a "isobutanol - water" mixture (irregular curve) and the non-stochastic contribution $\delta\tilde{T}_b$ (smooth curve), which contains two harmonics and described by the following equation:

$$\delta\tilde{T}_b = 0.461\cdot\sin(\pi n) + 0.323\cdot\sin(2\pi n)$$

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РЕГРЕССИОННЫЙ АНАЛИЗ ИЗОБАР ТЕМПЕРАТУРЫ КИПЕНИЯ ВОДНО-ОРГАНИЧЕСКИХ БИНАРНЫХ СМЕСЕЙ

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Воронежский государственный технический университет, ул. 20-летия Октября, 84, 394006 Воронеж, Россия
e-mail: robi57@mail.ru

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Аннотация. Построен алгоритм выделения детерминированного вклада в эмпирические зависимости физико-химических свойств бинарных водно-органических растворов от концентрации компонентов. Показано, что выделение неаддитивной части зависимости физико-химических характеристик от концентрации компонентов позволяет сформулировать алгоритм аналитического продолжения в формальную область отрицательных концентраций с непрерывными функциями, а также первой и второй производными. Сформулированы количественные критерии разделения стохастических и динамических гармоник в трехпараметрическое регрессионное описание изобар температуры кипения бинарных растворов. Сформулированы методы оптимизации алгоритма сглаживания эмпирических данных, уменьшающие объем необходимой информации. Построен базис регрессионного описания зависимости температуры кипения бинарных водно-органических растворов от состава, позволяющий учесть основной вклад в детерминированную часть эмпирической информации. Для ряда растворов рассчитан стохастический вклад в эмпирические данные. Показано, что ошибка предложенной регрессионной модели не превышает 2 % и определяется только экспериментальными погрешностями.

Ключевые слова: гомогенные смеси, вода, органические растворители, изобары, температура кипения, разложение Фурье.

Преображенский Михаил Артемьевич – к. ф.-м. н., доцент кафедры физики, Воронежский государственный технический университет; e-mail: pre4067@yandex.ru

Preobrazhenskii Mikhail A. – Cand. Sci. (Phys.-Math.), Assistant Professor of Physics Department, Voronezh State Technical University; e-mail: pre4067@yandex.ru

Рудаков Олег Борисович – д. х. н., профессор, заведующий кафедрой химии, Воронежский государственный технический университет; e-mail: robi57@mail.ru

Попова Марина Ивановна **–** аспирант кафедры химии, Воронежский государственный технический университет; e-mail: marinapopova1988@gmail.com

Rudakov Oleg B. – Dr. Sc. (Chem.), Professor, Head of Chemistry Department, Voronezh State Technical University; e-mail: robi57@mail.ru

Popova Marina I. **-** postgraduate student of Chemistry Department, Voronezh State Technical University; e-mail: marinapopova1988@gmail.com