ISOLATION OF DETERMINED COMPONENT OF EMPIRICAL DEPENDENCES OF PHYSICOCHEMICAL PROPERTIES OF BINARY SOLUTIONS ON THE COMPOSITION

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SUMMARY

An algorithm for separating deterministic and stochastic contribution to the empirical dependence of physicochemical properties of binary solutions on concentrations of the components based on the expansion of the function in a Fourier series has been done in this study. The isolation of a non-additive part of dependence of physicochemical characteristics on concentration of the components in the solution gives a possibility to formulate the algorithm of analytical continuation to the formal negative values of concentrations that make no break to the function and its first and second derivatives. The criteria of qualitative separation of deterministic and stochastic harmonics and the basic set of three-parameter regression description of isobar boiling point of binary solution have been determined. Two-stage algorithm of regressive description of dependence of boiling point of binary aqueous-organic solutions on composition has been formulated. The calculations of the contribution and number of stochastic determined harmonics in the experimental data for aqueous-organic solutions, which have a great practical importance, are shown in this work. It was found that the relative error of the proposed regressive model does not exceed 2% and can be defined only by experimental errors.

Keywords: *physicochemical properties, binary solutions, isolation, algorithm, Fourier series*

The dependence of the properties of the composition of the solutions has always attracted considerable interest, as determined by the role of these systems in engineering and applied chemistry [6]. Despite considerable interest to the description of solvation processes, there is no concept, which is capable to explain "ab initio" the observed phenomena and predict new phenomena [1]. Practical methods for the quantitative description of real multicomponent systems are based on the direct regression approximation of empirical data [4]. Error regression description contains two components with fundamentally different minimization methods.

Firstly, there are errors which related to the properties of the basis set of regression and determination accuracy of calculation the set's parameters. These errors can be made arbitrarily small.

Secondly, not only the reduction, but the evaluation of experimental error, is a complex task. Considerable scatter of experimental results, which is observed for the binary solutions [5], shows the stochastic contribution to the empirical results. However, in most of the experimental studies the evaluation of accuracy and stability of the experimental data is missed [5]. But the ratio of deterministic and stochastic component defines the boundaries of regression describing basis size. The purpose of this work is to develop methods for isolation of stochastic component of empirical array and to optimize the parameters based on the regression basis set.

The principle for separation examined dependence on deterministic and stochastic parts is based on the expansion of the function in a Fourier series [7].

$$X(n) = \sum_{m=1}^{\infty} b_i \sin(\pi\, m\, n) + \sum_{m=0}^{\infty} c_i \cos(\pi\, m\, n) \quad (1)$$

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Since the domain of the decomposition (1) $n \in [-1,1]$ misalign physically admissible domain $n \in [0,1]$, the analytic continuation of the function *X (n)* to the formal area of negative values of *n* is necessary.

The partial sums of the series (1) and Chebyshev polynomials are widely used in the description of regression in many scientific fields, including chemistry [7]. As it was shown in [2], the Fourier components (1) of continuous function, the first derivative of that function has discontinuity, decrease with the rate m^{-2}. Different behavior of the Fourier coefficients allows us to solve the problem of isolation the expansion terms (1), which describe the deterministic part of the empirical data.

However, the direct use of the expansion (1) for the description of physical and chemical experiments is usually impossible. Calculation of M Fourier coefficients of the expansion of functions, which is just a part of deterministic signal description, is possible only with set of M values of functions [2]. Finding of non-stochastic dependence on background of stochastic noise requires additional information. Specificity of physicochemical experiments does not provide a sufficient amount of data. Accordingly, development of algorithms for smoothing sets of experimental data considering specificity physicochemical experiments is needed. The solution of this problem is the aim of the current work. Dependency of isobars boiling temperature of binary aqueous-organic solutions on concentrations *T (n)* serves as an example of algorithm construction in present work. However, the application field of that algorithm is much wider.

For an 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 discontinuity of the function. Isolation of non - additive part $\Delta T(n)$ of the dependency $X(n)$ allows us to solve the problem for a binary homogeneous solution:

$$\Delta T(n) = T(n) - [T_1 n + T_2(1-n)] \quad (2)$$

Here, T_1 and T_2 are the boiling points of the individual components. Since $\Delta T(n)$ function takes zero value on the boundary domain, it can be analytically continued into the formal area $n \in [-1, 0)$ as an uneven function with continuous first and second derivatives. Consequently, non-stochastic terms of the Fourier series expansion portion (1) decrease at least as m^{-3}. This rate decrease makes very sharp difference between analysis and stochastic components behavior. The deterministic part of the expansion (1) the main contribution to the small number of components:

$$\Delta T_{\text{det}}(n) = \sum_{m=1}^{M} b_m \sin(\pi\, m\, n) \quad (3)$$

The expansion terms (1) with $m \square M$ describe the stochastic contribution. In the expansion (2) it is taken into account that the terms proportional to even function *cos(πmn)* takes zero value, which further reduces the amount of necessary empirical information in 2 times.

The number of determined harmonics *M* and sum coefficients (2) can be obtained directly from the experimental data. For K equidistant observations on the interval [0.1] the calculation of coefficients of the expansion (2) has the form [2]:

$$b_m = \frac{2}{K} \sum_{k=0}^{K} \Delta T\left(\frac{k}{K}\right) \sin\left(\frac{k\pi\, m}{K}\right) \quad (4)$$

In the idealized case of absence of noise all the coefficients of the expansion (1) starting from b_{M+1} take a negligible value. Therefore, the sum (3) not only describes the behavior of the system in the experimental points, but also allows us to interpolate the function ΔT(n) at all points of the domain [0.1]. The error of that interpolation at any point does not exceed the coefficient modulus b_M [2]. The presence

of random noise totally changes the situation. For all harmonics with m□M random alternation of signs of the coefficients b_m is observed without their modules reduction. Therefore, for this part of the spectrum parameter χ, defined by the formula

$$\chi_{jk} = \frac{1}{k}\sum_{m=M+j}^{M+j+k} b_m^2 \qquad (5)$$

remains constant with change of the lower boundary of summation and the number of terms taken into account.

Regression description algorithm of deterministic information part, based on the account of the studied system symmetry properties, allows making an additional reduction the number of necessary experimental data as proposed in [3, 4]. The modified algorithm is based on a description of the main functions of the determined contribution. The function form is determined by the described characteristics. Regression bases of isotherms density, dynamic viscosity and the surface tension and refractive index are obtained in [4]. Three-parameter basis isobars boiling points obtained in [7] has the form:

$$\Delta T_{\text{inv}} = \Delta T_e \cdot \sin\left[\frac{\pi}{2}\frac{1-\exp(-\alpha\, n)}{1-\exp(-\alpha)} + \left[\frac{1}{2} + \frac{\arctan 10^3 (n-n_e)}{\pi}\right]\frac{\pi}{2}\frac{n-n_e}{1-n_e}\right] \qquad (6)$$

Fourier decomposition (2) is constructed only for the difference $\delta T = \Delta T - \Delta T_{\text{inv}}$. Since the main part deterministic information is displayed by function ΔT_{inv}, the number of determined harmonics in the expansion difference is small, and as calculation results show, real experimental arrays [5] allow carrying out an effective description and smoothing.

Table 1. *Calculated results of deterministic and stochastic contributions to the empirical dependence of water-organic solvents boiling points*

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
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

The calculation results of deterministic and stochastic contribution to empirical boiling points dependences of several water-organic solvents are given in the table. Data in the table are arranged in decrease of the number *M* and a parameter (5). Absolute and normalized to a maximum amendment RMS errors of approximation (6) (σ and σ_n respectively) are included. The

last column shows the normalized mean square error of approximation based on the deterministic terms of the Fourier decomposition.

As calculation results for the most studied water-organic solutions show, the approximation (6) completely describes the deterministic part of the empirical results and, consequently, the equalities: M = 0, $\sigma_f = \sigma_n$. For some systems, the approximation (6) can be verified by taking into account the deterministic harmonics of function δT. The harmonics number for all the analytic solutions does not exceed two. Because of this, very limited amount of empirical information allows us to construct an adequate description of the equilibrium binary systems, which accuracy is determined only by random experimental errors. Consideration of additional harmonics allows us to reduce the relative error of the regression to values not exceeding the value of 2×10^{-2} in 2 - 3 times. Therefore, its further reduction can only be achieved by reducing the experimental error.

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TÓM TẮT

XÁC ĐỊNH SỰ PHỤ THUỘC TÍNH CHẤT HÓA LÝ CỦA DUNG DỊCH NHỊ PHÂN VÀO THÀNH PHẦN DUNG DỊCH BẰNG PHƯƠNG PHÁP CÔ LẬP

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Trong nghiên cứu này, tính chất hóa lý của dung dịch nhị phân được xác định là có sự phụ thuộc vào tính chất của các thành phần trong dung dịch. Sự phụ thuộc này được xác định và được biểu diễn bằng một thuật toán triển khai hàm mở rộng của chuỗi Fourier. Để tính toán và định lượng chính xác được sự đóng góp của các thành phần vào tính chất của dung dịch nhị phân thì các tác giả đã sử dụng phương pháp cô lập từng thành phần và thực nghiệm kiểm tra các tham số của các tính chất. Trong nghiên cứu đã chỉ ra ý nghĩa quan trọng cho việc xác định định lượng sự đóng góp của các thành phần vào tính chất hóa lý chung của dung dịch nhị phân. Sai số tương đối của phương pháp nghiên cứu này là nhỏ hơn 2% và được xác định là sai số thực nghiệm.

Từ khóa: *tính chất hóa lý, dung dịch nhị phân, cô lập, thuật toán, chuỗi Fourier.*

Ngày nhận bài: 20/6/2017; Ngày phản biện: 17/7/2017; Ngày duyệt đăng: 30/9/2017

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