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Splines in physicochemical studies of liquid binary mixtures

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Physicochemical studies of the organic-water mixtures show that their properties are not linear functions of their concentration but depend on the mixture composition in various ways. The evaluation of the measurement results requires an interpolation of the experimental data and the derivatives of a mixture property with respect to concentration should be known as well. The results of measurements are disturbed by experimental error which causes the scatter of the approximated function values and oscillations of the approximating function derivatives. In the paper an application of the 3^{rd} degree splines for the calculation of derivative and the interpolation for a non-uniform mesh are considered. Smoothing methods of an approximating function by means of splines are proposed. Some numerical examples illustrating the efficiency of the smoothing method and its applications are presented.

Keywords: splines, approximation, smoothing

1. Introduction

Physicochemical properties of ideal solution are linear functions of its concentration. But the properties of real solutions are usually nonadditive and depend on a solute concentration in various ways. Some examples of such relations are presented in Fig. 1. Graphs a, b, c, d show density, refractive index, speed of sound and viscosity, respectively, of some organic-water mixture as functions of its composition. Molecular interactions in mixtures differ from those in pure liquids and this is generally assumed a cause of deviations from ideal behaviour of solutions. But it is still not clear why some of these properties change monotonously when the mixture composition changes and others have maxima. Appearing of a maximum may be related to a specific structure of a solution in a given range of concentrations. In order to explain the relation between mixture properties and its structure, the responsibility of the particular component for the deviation of the system from ideality should be determined. So called "partial specific property" of the component may be calculated if the derivative of this mixture property with respect to concentration is known. Let $y = f(x)$ represent a function dependence of some property of the binary mixture A–B on the concentration x of B-component. Then according to the tangent line method the partial specific property of A-component (y_A) at the concentration value x_1 is equal to $y_A = x_1 \mathrm{d}y/\mathrm{d}x + y_1$ and the partial specific property of B is $y_B = x_1 \mathrm{d}y/\mathrm{d}x + y_1 + \mathrm{d}y/\mathrm{d}x$. The most popular method applied in such studies is a polynomial fitting to experimental points. However, obtained in this way the derivative dependence on concentration may be different for different polynomial degrees (Fig. 2).

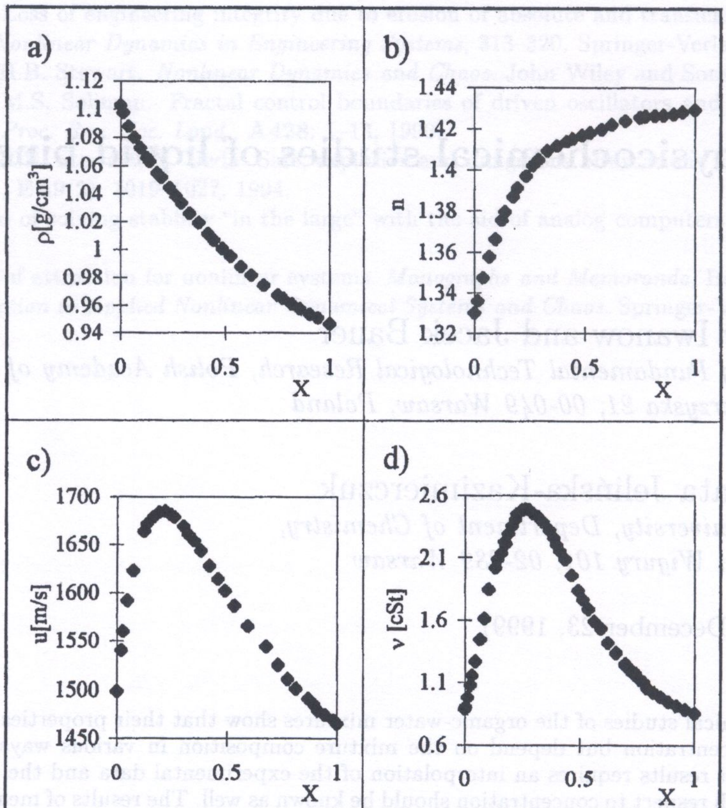

Fig. 1. Concentration dependence of the physicochemical properties; a) density, b) refractive index, c) speed of sound, d) viscosity

Some problems related to the molecular interactions (especially in water — organic mixtures) are expected to be solved by using the hydrogen isotope substitution. The experimental data (for instance viscosity measurements) obtained for regular and deuterated systems are compared and differences between them called isotope effects (for instance "the isotope effect of viscosity") are determined. Then their concentration dependences should be analyzed. A direct comparison of data obtained for regular and deuterated solutions can be made when measurements are carried out at the same concentration for both systems. But it is practically impossible to prepare the samples of both mixtures having exactly the same composition so an interpolation of the experimental data is necessary.

In the present paper an application of the 3rd degree splines for the calculation of derivative and the interpolation are described.

Spline application is not new [1] but in this particular case a nonstandard approach is developed on uniform mesh, like in the paper [2], for two-dimensional problems, and transformed to a non-uniform mesh determined by points from the domain of the independent variable x. Another problem which we face with is the fact that function values obtained from a measurement contain a noise (disturbance of these values) due to experimental error. Real and approximated values are of course, very close, according to the theorems of the spline theory, but approximated values of derivatives are quite often very far from exact derivative values of the non-disturbed function. Smoothing of an approximating function also by means of splines is a main aim of the present paper.

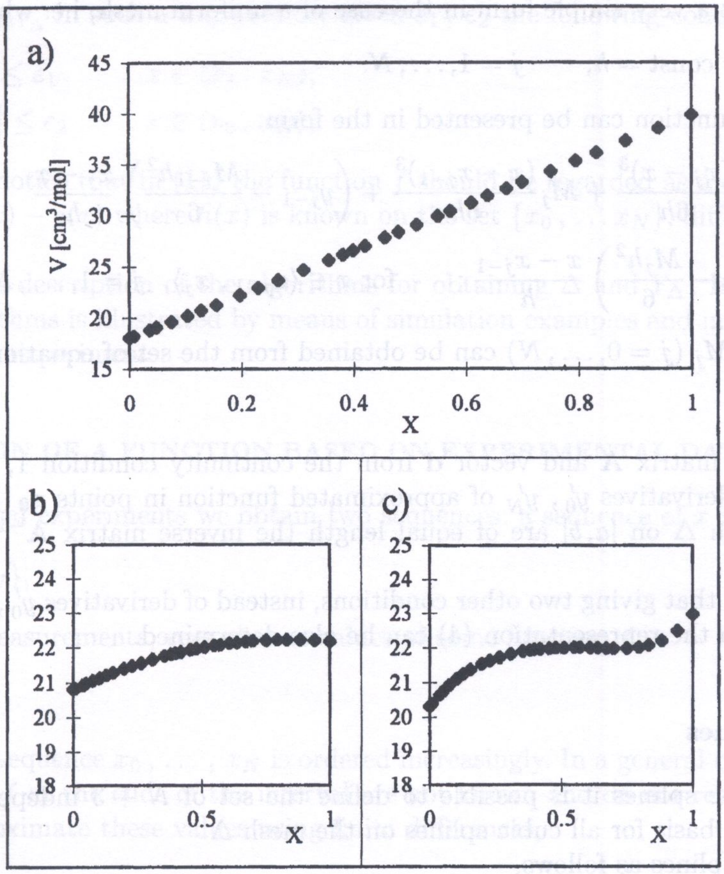

Fig. 2. a) The average molar volume of the liquid binary mixture; b) 3rd degree polynomial derivative, c) 6th degree polynomial derivative

2. Fundamental notions on splines [3]

2.1. The spline of 3rd degree

Let us consider an interval $\langle a, b\rangle$ and its division

$$\Delta : \quad a = x_0 < x_1 < \ldots < x_N = b. \tag{1}$$

Let a sequence of values be given

$$Y : \quad y_0\,, y_1\,, \ldots, y_N\,. \tag{2}$$

The function $S_{\Delta Y}$ is said to be a *spline* of a 3rd degree (cubic spline) if it satisfies the following conditions:

1. $S_{\Delta Y}$ is continuous together with its first and second derivatives on the interval $\langle a, b\rangle$.

2. On each interval $\langle x_i\,, x_{i+1}\rangle$, $i = 0, 1, \ldots, N-1$, $S_{\Delta Y}$ is a polynomial of 3rd degree.

3. $S_{\Delta Y}(x_j) = y_j$, $j = 0, \ldots, N$.

This function has a very simple form in the case of a uniform mesh, i.e. when

$$h_j = x_j - x_{j-1} = \text{const} = h; \qquad j = 1, \dots, N. \tag{3}$$

The approximated function can be presented in the form

$$S_{\Delta Y}(x) = M_{j-1}\frac{(x_j - x)^3}{6h} + M_j\frac{(x - x_{j-1})^3}{6h} + \left(y_{j-1} - \frac{M_{j-1}h^2}{6}\right)\frac{x_j - x}{h} + \left(y_j - \frac{M_j h^2}{6}\right)\frac{x - x_{j-1}}{h}; \qquad \text{for } x \in \langle x_{j-1}, x_j\rangle,\ j = 1, \dots, N. \tag{4}$$

The parameters M_j $(j = 0, \dots, N)$ can be obtained from the set of equations

$$\mathbf{A} \cdot \mathbf{M} = \mathbf{d}. \tag{5}$$

One can obtain the matrix $\mathbf{A}$ and vector $\mathbf{d}$ from the continuity condition 1, the condition 3 and assuming values of derivatives y'_0, y'_N of approximated function in points x_0, x_N. In the case the intervals of the mesh Δ on $[a, b]$ are of equal length the inverse matrix $\mathbf{A}^{-1}$ can be determined analytically.

One has to notice that giving two other conditions, instead of derivatives y'_0, y'_N, the parameters M_j, $j = 0, \dots, N$, in the representation (4) can be also determined.

2.2. Cardinal splines

In the space of cubic splines it is possible to define the set of $N + 3$ independent splines called *cardinal* that form a basis for all cubic splines on the mesh Δ.

Denote cardinal splines as follows,

$$A_{\Delta,k}(x), \quad k = 0, 1, \dots, N; \qquad B_{\Delta,l}(x), l = 0, N. \tag{6}$$

The parameters which are necessary for determination of the splines are obtained in the following way,

$$\begin{aligned} &A_{\Delta,k}(x_j) = \delta_{kj}, \quad j = 0, 1, \dots, N; \qquad A'_{\Delta,k}(x_i) = 0, \quad i = 0, N, \quad k = 0, 1, \dots, N \\ &B_{\Delta,l}(x_j) = 0, \quad j = 0, 1, \dots, N; \qquad B'_{\Delta,l}(x_i) = \delta_{li}, \quad i = 0, N, \quad l = 0, N. \end{aligned} \tag{7}$$

Using cardinal splines we can express an arbitrary spline function of one variable in the interval $\langle a, b\rangle$ with given division Δ, by means of their linear combination,

$$S_{\Delta Y}(x) = \sum_{j=0}^{N} A_{\Delta,j}(x)\, y(x_j) + y'(a)\, B_{\Delta,0}(x) + y'(b)\, B_{\Delta,N}(x). \tag{8}$$

3. Problem formulation

Our problem can be formulated as follows. Let $f(x) \in C^1$, $x \in \langle x_0, x_N\rangle$ be a function which has to be approximated on the interval $\langle x_0, x_N\rangle$ and $g(x)$ is a function with random values e.g. experimental errors in the interval $\langle x_0, x_N\rangle$. Values of a function $h(x) = f(x) + g(x)$ are known on a discrete set of variable x, $\{x_0, \dots, x_N\}$ i.e. $\{h(x_0), \dots, h(x_N)\}$.

The aim is to find a mesh Δ of points in the interval $\langle x_0, x_N\rangle$

$$\Delta = \{x_0^\Delta = x_0, \dots, x_N^\Delta = x_N\}, \tag{9}$$

and assigned with them values

$$Y_\Delta = \{y_0^\Delta, \dots, y_N^\Delta\} \tag{10}$$

and a cubic spline $S_{\Delta Y_\Delta}$ in such a way that for given $\varepsilon_1, \varepsilon_2$ the following conditions

$$|f(x) - S_{\Delta Y_\Delta}(x)| \le \varepsilon_1 \qquad x \in \langle x_0, x_N\rangle, \tag{11}$$

$$|f'(x) - S'_{\Delta Y_\Delta}(x)| \le \varepsilon_2 \qquad x \in \langle x_0, x_N\rangle, \tag{12}$$

are satisfied. Let us notice that in (11) the function f should be regarded as a difference between h and g i.e. $f(x) = h(x) - g(x)$ where $h(x)$ is known on the set $\{x_0, \dots x_N\}$, different from the mesh Δ in (9).

Section 5 contains description of the algorithms for obtaining Δ and Y_Δ. In Section 6 an effectiveness of the algorithms is illustrated by means of simulation examples and in a treatment of data obtained in chemical experiments.

4. APPROXIMATION OF A FUNCTION BASED ON EXPERIMENTAL DATA

As a result of chemical experiments we obtain two sequences: a sequence of x values,

$$X = \{x_0, \dots, x_N\}, \tag{13}$$

and a sequence of measurements, regarded as values of some function f,

$$Y = \{y_0, \dots, y_N\}. \tag{14}$$

We assume that the sequence $x_0, \dots, x_N$ is ordered increasingly. In a general case values of derivatives of the function f at the ends of the interval are not known and do not result from a measurement. One can approximate these values using finite differences,

$$y'_0 = \frac{y_1 - y_0}{x_1 - x_0}, \qquad y'_N = \frac{y_N - y_{N-1}}{x_N - x_{N-1}}. \tag{15}$$

It is seen that in a general case the mesh X is a non-uniform thus the condition (3) is not satisfied. One can use the procedure analogous to that described in the paper [2] for two-dimensional problems. We will follow this and define the mesh

$$R = \{r_0, r_1, \dots, r_N\} \quad \text{with} \quad r_i = r_0 + i\,\frac{r_N - r_0}{N}, \quad i = 0, \dots, N; \quad r_0 < r_N, \tag{16}$$

where r_0, r_N — arbitrary (algorithm) parameters which are not related to x_0 and x_N, and associate to it the sequence of values (14) as well as values of derivatives

$$y'_{0S} = \frac{y_1 - y_0}{r_1 - r_0} \quad \text{and} \quad y'_{NS} = \frac{y_N - y_{N-1}}{r_N - r_{N-1}}. \tag{17}$$

Having (16), (14), (17) one can determine spline

$$S_{RY}(r), \qquad r \in \langle r_0, r_N\rangle, \tag{18}$$

by means of the relation (8).

Now we determine a spline $S_{RX}(r)$ which will realize a transformation of the interval $\langle r_0, r_N\rangle$ of the variable r into interval $\langle x_0, x_N\rangle$ of the variable x such that nodes of the mesh (16) translate to nodes of the mesh (13)

$$r_i \to x_i, \qquad i = 0, \dots, N. \tag{19}$$

For this transformation the mesh $R = \{r_0, \dots, r_N\}$ plays the role of the mesh Δ in (8) while the sequence of x values from (13), i.e. $X = \{x_0, \dots, x_N\}$ gives values x_i of the spline $S_{RX}(r)$ at nodes r_i for $i = 0, \dots, N$.

Hence from (8) taking $\Delta \equiv R, Y \equiv X, x \equiv r$ and derivatives on ends of the interval equal

$$x'_0 = \frac{x_1 - x_0}{r_1 - r_0}, \qquad x'_N = \frac{x_N - x_{N-1}}{r_N - r_{N-1}}, \tag{20}$$

one obtains the spline $S_{RX}(r)$. This spline is called the *spline transformation.*

Using (18) the approximation function f can be determined by

$$f(x) = f(S_{RX}(r)) = S_{RY}(r). \tag{21}$$

The above function enables us to approximate derivative of the measured function

$$f'(x) = \frac{S'_{RY}(r)}{S'_{RX}(r)}, \tag{22}$$

provided that the derivative $S'_{RX}(r)$ does not vanish.

In order to use practically relations (21) and (22), it is necessary to determine $S_{RX}^{-1}(x)$ or for given x to find r associated to it. Now the problem is to find, for a given value of $x \in \langle x_0, x_N \rangle$ such a value of $r \in \langle r_0, r_N \rangle$ that the condition $S_{RX}(r) = x$ is satisfied. The bisection method [4] can be used to solving this problem. The possible algorithm of the method could be:

1. find i and the corresponding subinterval $\langle x_i, x_{i+1} \rangle$ for which $x \in \langle x_i, x_{i+1} \rangle$;

2. according to the transformation of $\langle r_0, r_N \rangle$ into $\langle x_0, x_N \rangle$ realized by the spline S_{RX} the subinterval $\langle x_i, x_{i+1} \rangle$ is the image of the subinterval $\langle r_i, r_{i+1} \rangle$;

3. find in the subinterval $\langle r_i, r_{i+1} \rangle$ by means of the bisection method the value r which approximates x with given exactness ε, $|x - S_{RX}(r)| \le \varepsilon$.

The algorithm converges very fast.

5. Smoothing of an approximating function

The approximation method presented above is sufficient if for further investigations only values of the function are needed. The problem is much more complex when one needs to approximate the derivative of the function. Let us illustrate this problem using the function shown on Fig. 3a. The values with some experimental error measured in successive points are marked by squares. Continuous line is a graph of the fitted function. Due to the fact that the spline approximation goes through all points, its derivative (dotted line) shows significant oscillations and probably a large deviation from its real shape. Increasing number of experimental points does not solve the problem. The method of smoothing of the function approximation is illustrated in Fig. 3b. Experimental points are marked by squares joined by a spline function (dotted line). The values of the function approximation in mid-points between adjacent measurement points are marked by $\times$. It seems that if in the next step one changes the approximation mesh and takes values from these points as a basis to the next function approximation it is possible to obtain a reduction in the deviation in the spline approximation of the derivative. Similar results may be obtained by using regular mesh with a variable number of points.

At last two algorithms have been realized:

1. by means of regular mesh with a variable number of division points (Sec. 5.1),

2. by means of mid-points of subintervals as a new mesh (Sec. 5.2).

Here the both algorithms are described.

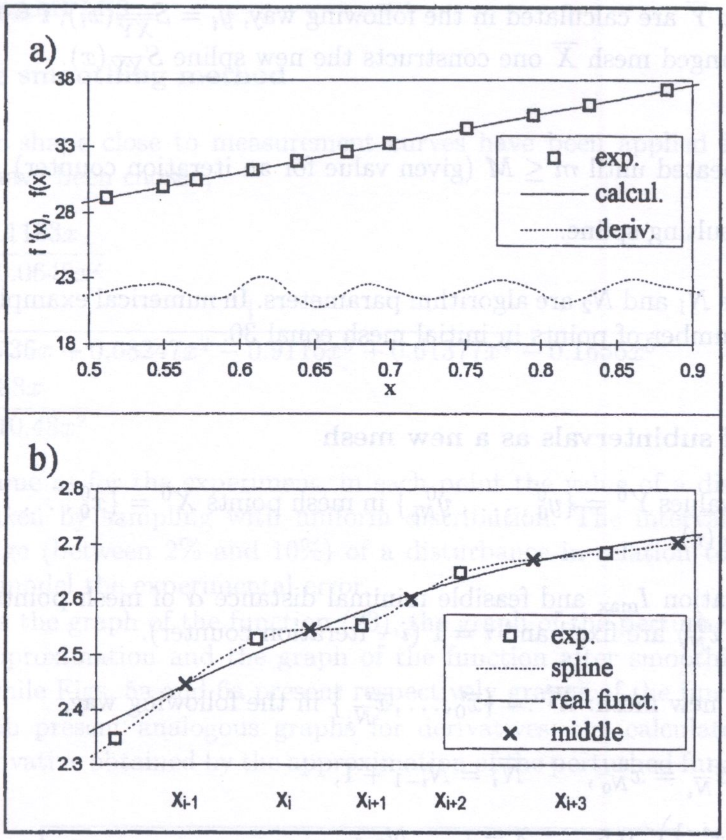

Fig. 3. a) Oscillation of the spline derivative, b) method of the smoothing

5.1. Regular mesh with a variable number of points

1. Using measured values $Y = \{y_0, \ldots, y_N\}$ in mesh points $X = \{x_0, \ldots, x_N\}$, one constructs the spline $S_{RY}(r)$.

2. On an uniform mesh with given number of points $N_1 + 1$ and $m = 0$ (m – iteration counter)

$$\overline{X} = \{\overline{x}_0 = x_0, \ldots, \overline{x}_{N_1} = x_N\}, \qquad \overline{x}_i = x_0 + i\,\frac{x_N - x_0}{N_1}, \qquad i = 0, \ldots, N_1,$$

assuming

$$\overline{Y} = \{\overline{y}_0, \ldots, \overline{y}_{N_1}\} \qquad \text{where} \qquad \overline{y}_i = S_{RY}(\overline{r}_i), \quad \overline{r}_i = S^{-1}_{RX}(\overline{x}_i),$$

one constructs the next spline $S_{\overline{XY}}(x)$.

3. On the other uniform mesh with given number of points $N_2 + 1$ ($N_2 \neq N_1$)

$$\overline{\overline{X}} = \{\overline{\overline{x}}_0 = x_0, \ldots, \overline{\overline{x}}_{N_2} = x_N\}, \qquad \overline{\overline{x}}_i = x_0 + i\,\frac{x_N - x_0}{N_2}, \qquad i = 0, \ldots, N_2,$$

assuming

$$\overline{\overline{Y}} = \{\overline{\overline{y}}_0, \ldots, \overline{\overline{y}}_{N_2}\} \qquad \text{where} \qquad \overline{\overline{y}}_i = S_{\overline{XY}}(\overline{\overline{x}}_i),$$

one constructs the spline $S_{\overline{\overline{XY}}}(x_i)$.

4. The new values in $\overline{Y}$ are calculated in the following way, $\overline{y}_i = S_{\overline{\overline{XY}}}(\overline{x}_i)$, $i = 0, \ldots, N_1$. Using the new $\overline{Y}$ and unchanged mesh $\overline{X}$ one constructs the new spline $S_{\overline{XY}}(x)$.
5. $m := m + 1$

   Steps 3–5 are repeated until $m \leq M$ (given value for an iteration counter)
6. $S_{\overline{XY}}(x)$ is the resulting spline.

Numbers of points N_1 and N_2 are algorithm parameters. In numerical examples $N_1 = 30$, $N_2 = 40$ are assumed, with number of points in initial mesh equal 30.

5.2. Mid-points of subintervals as a new mesh

1. Using measured values $Y^0 = \{y_0^0, \ldots, y_{N_0}^0\}$ in mesh points $X^0 = \{x_0^0, \ldots, x_{N_0}^0\}$ one constructs the spline : $S_{R^0Y^0}(r)$.
2. A number of iteration $I_{\max}$ and feasible minimal distance α of mesh points from end points of the interval $\langle x_0^0, x_N^0\rangle$ are fixed and $i = 1$ (i – iteration counter).
3. One constructs a new mesh: $\overline{X}^i := \{\overline{x}_0^i, \ldots, \overline{x}_{\overline{N}_i}^i\}$ in the following way,
$$\overline{x}_0^i = x_0^0, \qquad \overline{x}_{\overline{N}_i}^i = x_{N_0}^0, \qquad \overline{N}_i = N_{i-1} + 1,$$
$$\overline{x}_j^i = \left(x_{j-1}^{i-1} + x_j^{i-1}\right) \cdot 0.5, \qquad j = 1, \ldots N_{i-1}.$$
   The set $\overline{X}^i$ contains boundary points of the considered interval and mid-points (centers) of a previous iteration steps.
4. The points for which the distance from boundaries interval is less than α are eliminated from the set $\overline{X}^i$
$$X^i = \left\{x : \quad x \in \overline{X}^i; \ |x - x_0^0| \geq \alpha \ \wedge \ |x - x_{N_0}^0| \geq \alpha\right\} \cup \{x_0, x_N\}.$$
   The new set is denoted by $X^i = \{x_0^i, \ldots, x_{N_i}^i\}$.
5. $Y^i = \{y_0^i, \ldots, y_{N_i}^i\}$ where $y_j^i = S_{R^{i-1}Y^{i-1}}(r_j)$; $r_j = S^{-1}_{R^{i-1}X^{i-1}}(x_j^i)$, $j = 0, \ldots, N_i$ are determined.
6. $i := i + 1$
7. If $i < I_{\max}$ go to 3 else STOP.
8. The required splines are $S_{R^IY^I}(r)$ and $S_{R^IX^I}(r)$.

The functions and their derivatives approximated according to the algorithm are presented in Section 6.

Essential parameters of the above algorithm are α and the number of the iterations. In numerical examples, also in those which are not presented in the paper, it has been determined that the algorithm is convergent. Different systems of subinterval divisions than described above were also tested. It seems that the most efficient is of the mid-points algorithm. The above algorithms have a heuristic character but the numerical examples presented below show their efficiency.

6. Numerical examples

6.1. Testing of the smoothing method

Functions with their shape close to measurement curves have been applied for simulations. The following functions have been chosen,

$$y = \frac{1.0983 + 0.1183x}{1 + 0.35x - 0.0645x^2} \tag{23}$$

$$y = \frac{1}{0.7522 - 0.2736x + 0.68247x^2 - 0.9115x^3 + 0.61377x^4 - 0.1636x^5} \tag{24}$$

$$y = \frac{0.89 + 6.88x}{1 - 3.89x + 10.48x^2} \tag{25}$$

For the mesh, the same as for the experiment, in each point the value of a disturbance in a given interval has been taken by sampling with uniform distribution. The interval has been given by assuming a percentage (between 2% and 10%) of a disturbance in relation to calculated value of function in order to model the experimental error.

Figure 4a presents the graph of the function (23), the graph of the perturbed function (2%–6%) as initial date for approximation and the graph of the function after smoothing by means of the method (Sec. 5.2), while Figs. 5a and 6a present respectively graphs of the functions (24) and (25).

Figures 4b, 5b, 6b present analogous graphs for derivatives: the calculated derivative of the original function, derivative obtained by the approximation of the perturbed function and derivatives

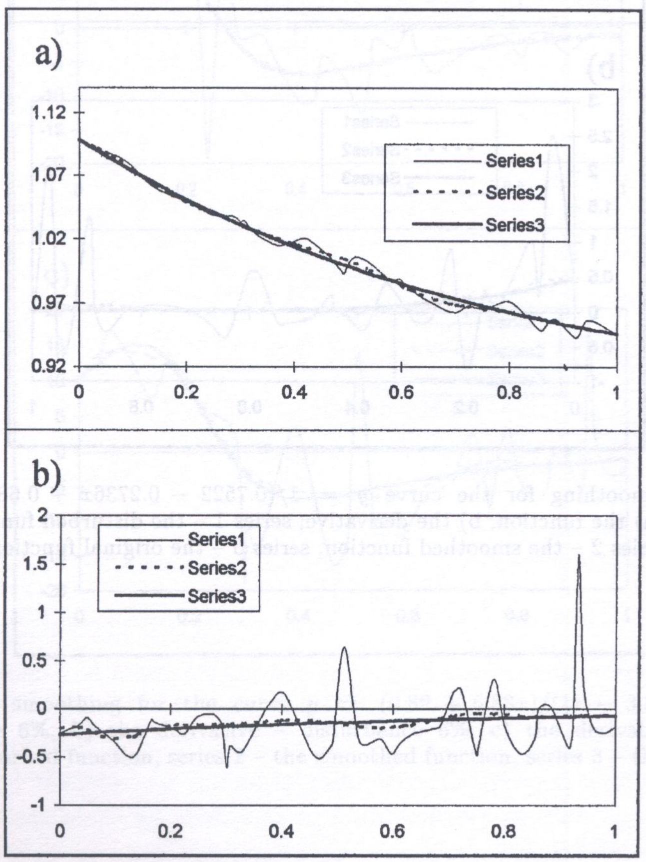

Fig. 4. Results of smoothing for the curve $y = (1.0983 + 0.1183x)/(1 + 0.35x - 0.0645x^2)$; a) the function, b) the derivative; series 1 – the disturbed function (disturbance 2%), series 2 – the smoothed function, series 3 – the original function

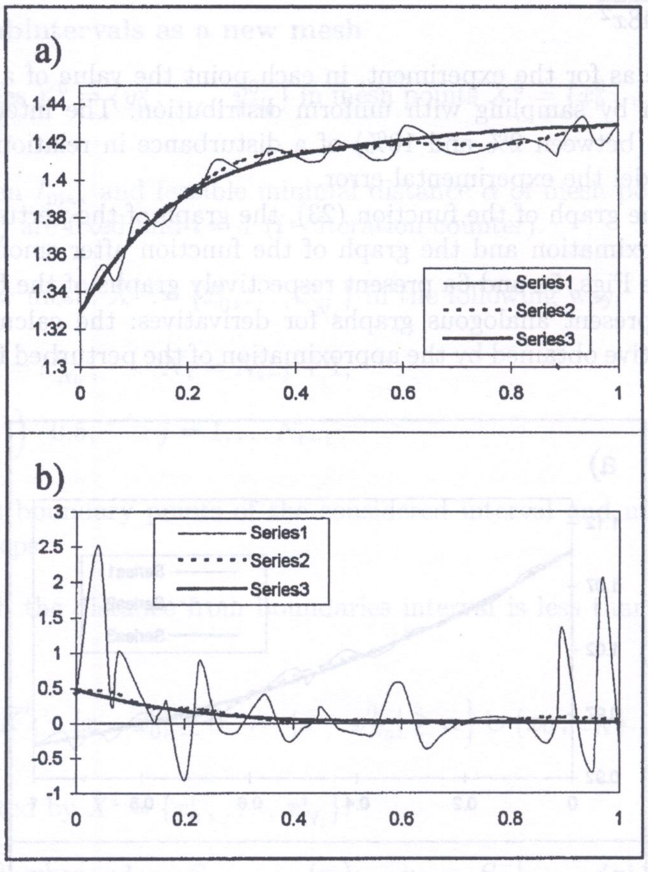

Fig. 5. Results of smoothing for the curve $y = 1/(0.7522 - 0.2736x + 0.68247x^2 - 0.911115x^3 + 0.61377x^4 - 0.1636x^5)$; a) the function, b) the derivative; series 1 – the disturbed function (disturbance 2%), series 2 – the smoothed function, series 3 – the original function

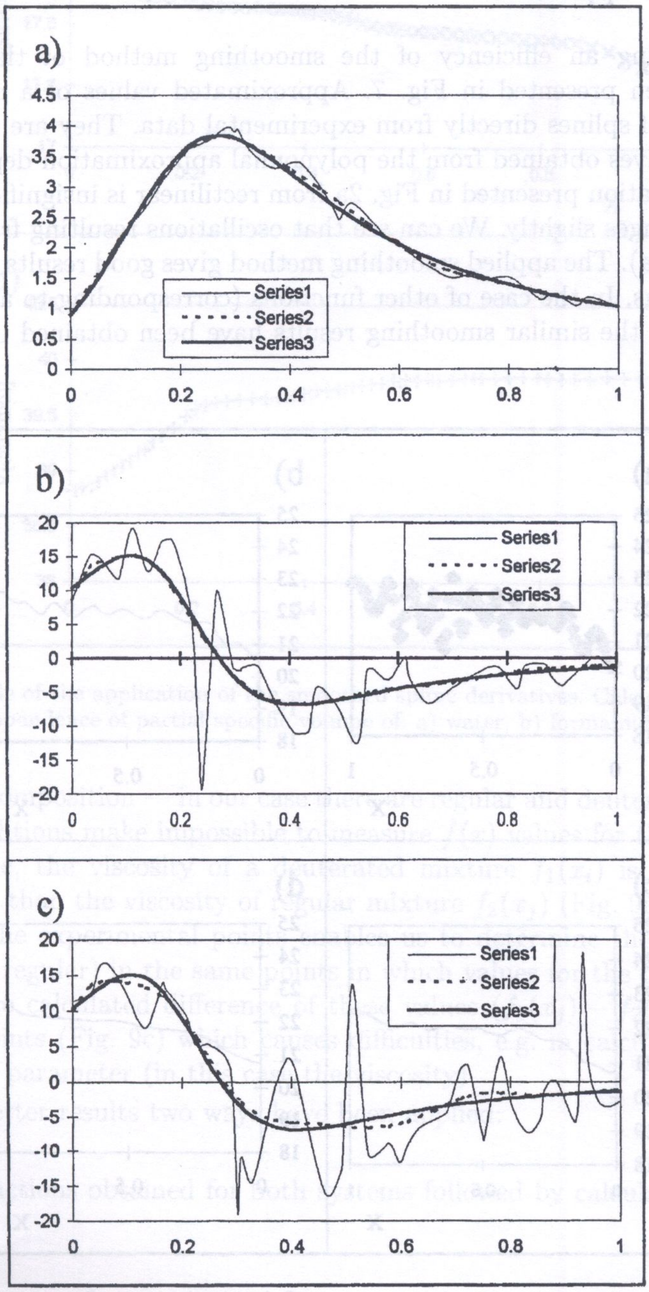

Fig. 6. Results for smoothing for the curve $y = (0.89 + 6.88x)/(11 - 3.89x + 10.48x^2)$; a) the function – disturbance 6%, b) the derivative – disturbance 6%, c) the derivative – disturbance 10%; series 1 – the disturbed function, series 2 – the smoothed function, series 3 – the original function

after smoothing. Additionally the efficiency of the smoothing of the derivative of the function (25) with 10% disturbance is presented in Fig. 6c.

It is evident, mainly in the case of derivatives that the smoothing is very efficient.

6.2. The examples of application

The example illustrating an efficiency of the smoothing method of the approximating function (Sec. 5.1) has been presented in Fig. 7. Approximated values of a derivative (Fig. 7a) are determined by means of splines directly from experimental data. They are presented in Fig. 2a. In Figs. 2b and 2c derivatives obtained from the polynomial approximation depend on the polynomial degree. Deviation of relation presented in Fig. 2a from rectilinear is insignificant thus the derivative in the whole range changes slightly. We can see that oscillations resulting from measurement errors are considerable (Fig. 7a). The applied smoothing method gives good results (Fig. 7b–d) but it needs more than 400 iterations. In the case of other functions (corresponding to another physicochemical properties of mixtures) the similar smoothing results have been obtained using no more than 600 iterations.

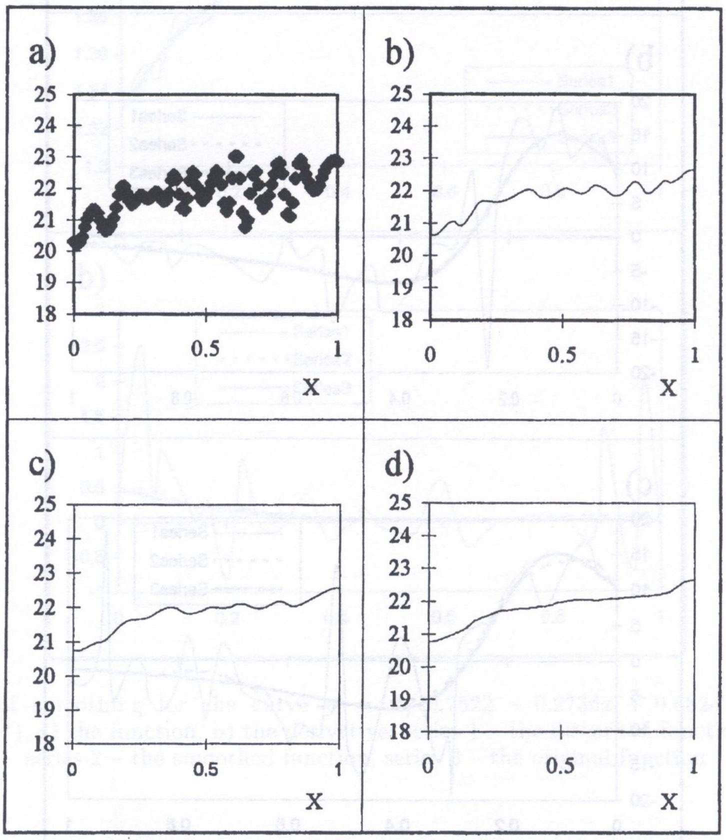

Fig. 7. Spline derivative smoothing effects; a) spline derivatives calculated for experimental points, b) after 100 iterations, c) after 200 iterations, d) after 600 iterations

Smoothed derivatives give a possibility of calculation of the relation between partial specific property for each component and its concentration in a mixture [5]. Calculation examples of "partial specific volume" are presented in Fig. 8.

For some cases the smoothing of a function approximation is necessary even if the elaboration of results does not need the derivative calculation. As an example we can show the method of isotope effects described in Introduction. It is based on the comparison of properties of the systems

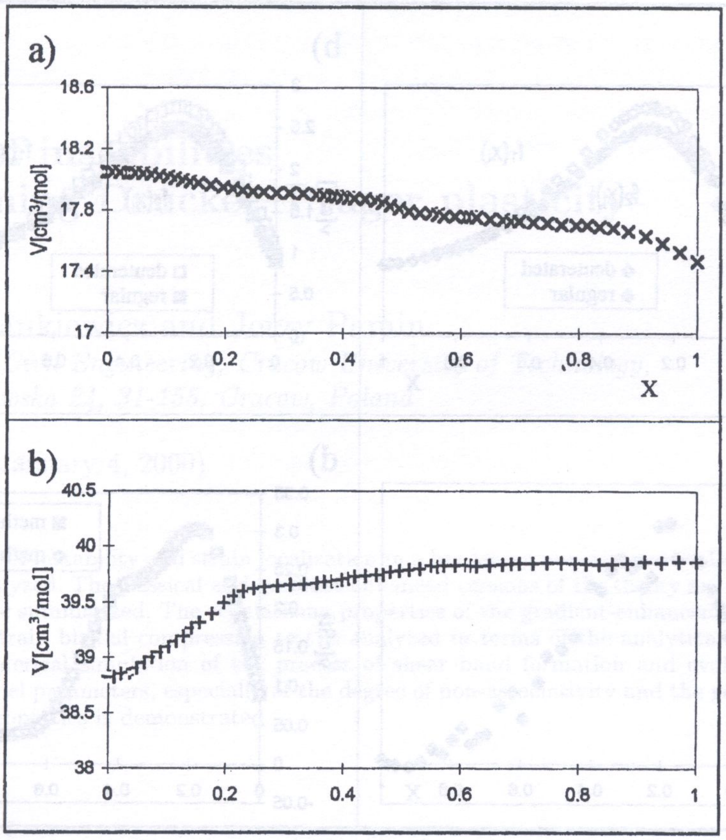

Fig. 8. The example of the application of the smoothed spline derivatives. Calculated concentration dependence of partial specific volume of: a) water, b) formamide

differing in the isotope composition — in our case there are regular and deuterated solutions. In most cases experimental conditions make impossible to measure $f(x)$ values for the same set of function arguments. For example, the viscosity of a deuterated mixture $f_1(x_i)$ is measured for different concentrations of solute than the viscosity of regular mixture $f_2(x_j)$ (Fig. 9a). Fitting of the spline function to the set of the experimental points enables us to determine the value of this function for a given system (e.g. regular) in the same points in which values for the deuterated system were measured (Fig. 9b). The calculated difference of these values $(f_1(x_j) - f_2(x_j))$ demonstrates the significant scatter of points (Fig. 9c) which causes difficulties, e.g. in calculations of the maximal isotope effect of a given parameter (in this case the viscosity).

In order to obtain better results two ways have been applied:

a) smoothing of the functions obtained for both systems followed by calculations of the difference between them,

b) calculation of a difference of approximated functions and smoothing the results.

Numerical results obtained for both cases differ insignificantly and curves corresponding to a difference $f_1(x_j) - f_2(x_j)$ obtained by means of two methods are practically the same (Fig. 9d).

We can say that the proposed algorithms are very efficient, mainly in the case of a derivative approximation. Direct spline approximation without smoothing is practically useless. As it is shown in the numerical examples presented in Sec. 6.1 the smoothing application enables us to obtain with a good approximation the original testing function and its derivative even with significant random distributions.

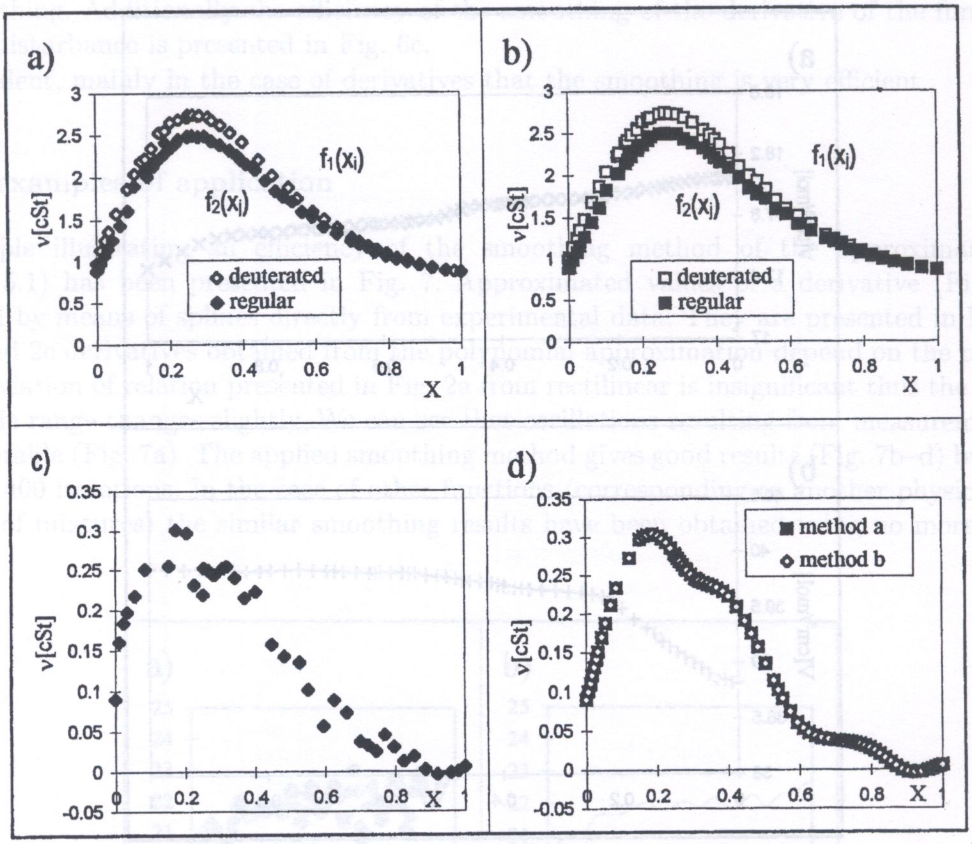

Fig. 9. The mixture viscosity isotope effect determination a) experimental data, b) interpolated values, c) the isotope effect calculated, d) the comparison of two methods

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