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COMPARISON OF 2-VARIABLE INTERPOLATION METHODS FOR PREDICTING THE VAPOUR PRESSURE OF AQUEOUS GLYCEROL SOLUTIONS

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Abstract: Several general mathematical methods for approximating two variable functions are applied for the study of the temperature - concentration - vapour pressure relation of aqueous glycerol solutions. The general properties of the applied methods are also discussed for possible other applications.

Keywords: approximation, splines, glycerol, aqueous solutions.

Introduction

Recently evaporation of aqueous solutions with small glycerol concentrations obtained from the combined processes of ion-exchange and chemisorption on diluted solutions is ever increasingly preferred instead of expensive purification of concentrated glycerol solutions required by the cosmetic industry [1], [2], [3]. During atmospheric evaporation of highly concentrated glycerol solutions the glycerol molecule can easily loss water and transforms into acrolein or polyglycerols, thus the control of the appropriate temperature limits is very important in the industrial scale technological processes.

In the present work mathematical relationships between concentration - vapour pressure - boiling point temperature thermodynamic data for aqueous glycerol solutions are studied. The possibilities of data interpolation with the application of several *two-variable* spline-interpolation methods are investigated with the aim of calculating low pressure evaporation conditions and upper temperature limits for aqueous glycerol solutions with given concentrations. We continue our former research announced in [4] and [5].

The data and the methods

We use the data in *Table 1*, taken from [6]**;** this dataset is illustrated in *Figure 1*.

Approximating a *two valued function* means that we are given the measured *values* $z_{i,j} \in \mathrm{R}$ at the measured *points* $P_{i,j} = (x_i, y_j)$ for $1<i<M$, $1<j<N$ and we want to construct a smooth function $S : \mathrm{R}^2 \to \mathrm{R}$ such that $S(x_i, y_j) = z_{i,j}$ for $1<i<M$, $1<j<N$.

In the present paper we considered the following well known general approximation methods:

- iterated 1 dimensional cubic splines,
- Hermite type 2 dimensional interpolation, improved by M. Lénárd (three versions),
- Shepard's generalized method for scattered dataset (with certain parameters, two versions).

These methods are general approximation methods, not only for the present problem. When discussing the errors of the computer outputs we try to separate their general mathematical and the chemical (material) specific reasons.

Our idea for testing the practical applicability of these methods is the following. We used every *second* column of the original dataset (*Table 1*, columns 0.0053, 0.0202, ... , 0.1013) for approximation input, then we computed the approximations for the omitted columns, and finally we compared the computed values to the measured data from *Table 1* at the omitted columns (0.0133, 0.0266, ..., 0.0933). These approximations and comparisons are shown in *Table 2* and are visualized on *Figures 2* to *6*. **Because of the large size of** *Table 2* **we publish it on our webpage [19].**

We do *not* deal with specific semiempirical formulas like in [7] :

$$\ln(p) = A(c) \cdot t^{a(c)},$$

where:

p – pressure (MPa),
c – concentration (%),
t – temperature (°C).

Iterated 1-Dimensional Interpolations

In [8] and [9] one finds the well known method of two variable spline interpolation which repeatedly uses one dimensional spline interpolations. (The details can be found in [2], too.) This method requires that the domain of the function we are approximating is a rectangle $[a,b]\times[c,d]$ and that the measured points $P_{i,j}$ lie on lines ℓ_j parallel to the ordinate axis for $1<j<N$. For calculating $S(x,y)$ at each inner point $(x,y)\in[a,b]\times[c,d]$ we follow a two-step calculation. First we use 1-dim. splines s_j in each horizontal line ℓ_j to compute the values $\ell_j(x,y_j) = s_j(x)$ for $1<j<N$. Next we use a further 1-dim. spline along the vertical line crossing the point (x,y), that is we calculate the value $S(x,y)$ using the numbers $\ell_j(x,y_j)$ for $1<j<N$ and a 1-dim. spline on them. (In practice we can compute all the formulae of the splines s_j in advance, so later the values of $s_j(x)$ can be obtained by an easy substitution.)

In our computations we used cubic splines (described in [2], [8] and [9]).

The approximating function $S(x,y)$ for our glycerol data is drawn in *Figure 2*, detailed numeric values can be found in [19].

Advantages of this method: the one-dimensional approximation method is widely known, no equidistance tabulated (measuring) points y_j or x_i are needed, only the parallel lines ℓ_j are assumed. The method also gives approximation at the margins of the closed rectangle $[a,b]\times[c,d]$. The method can be easily generalized for higher dimensions.

Disadvantages of this method: the repeated use of the final spline approximation ("vertical step") for getting $S(x,y)$ at each point (x,y) makes the computation (slightly) slower: we repeatedly have to build up and solve a tridiagonal $N\times N$ size system of linear equations.

Direct 2-Dimensional Interpolations

In [10] one can find simple but general direct 2-dimensional methods for constructing directly a two dimensional spline interpolation of minimal degree of *Hermite type*, invented by *M.Lénárd*. (She investigated 2- and more dimensional methods also in [11], [12], see also [2].)

This method requires the dataset (measuring points) form a rectangle-grid, i.e. each quadruple

$$\{ (x_i,y_j), (x_{i+1},y_j) (x_i,y_{j+1}) (x_{i+1},y_{j+1}) \} \qquad (1)$$

form a rectangle, not necessarily of the same size.
([11] requires equidistant grid, this problem is discussed in [2].) The method we currently use from [10] gives us separate formulae for each rectangle in (1) as

$$S(x,y) = S_{i,j}(x,y) \quad \text{if} \quad (x,y)\in[x_i,x_{i+1}]\times[y_j,y_{j+1}] \qquad (2)$$

such that finally we will have

(a) *S is twice continuously partially differerentiable in both variables on its whole domain* $[a,b]\times[c,d]$,

(b) *$S_{i,j}$ are polynomials in both variables of minimal degree* and *their degrees, as regarded as a two-variable polynomials, are minimal, too*.

Moreover, Lénárd provided *three* different formulae for (a)-(b), the details can be found in [10] in formulas (1,3), (2,3) and in (3,3). We implemented each of these three methods, detailed numeric values can be found in [19]. The difference among the approximating results of these three methods are not so significant, so we serve here the diagram of the first method in *Figure 3*.

Advantages of this method: Although the precomputation of the higher dimensional arrays takes some time, $S(x,y)$ can then be computed as a polynomial at any point (x,y), making the computation fast. Further, the method can be easily generalized for higher dimensions as described in [12].

Disadvantages of this method: We ultimately need rectangular tabulated (measuring) points $P_{i,j} = (x_i,y_j)$. (If required, the measuring points can be transformed to form equidistant grid, i.e. the rectangles in (1) to be congruent, see [2].) Further, the method gives no approximation at certain margins of the rectangle $[a,b]\times[c,d]$, since we can not compute the finite partial differences of higher order at the margin.

Shepard's Method

In [13] D. Shepard presented a more general method for continuous approximation in *any* dimension (his method is investigated e.g. in [14], [15], [16], [17], too.) This method does *not* require any special assumption on the positions of the measuring points $P_{i,j}\in R^n$: it works for *arbitrary distribution of the data points*.

This method can easily be introduced as follows.
Let the arbitrary measuring points

$$P_1, P_2, \ldots, P_M \in R^n$$

and the corresponding values

$$F_1, F_2, \ldots, F_M \in R$$

be given. Then the formula *for each* $P\in R^n$

$$U(P) = \frac{\sum_{i=1}^{M} F_i \cdot \sigma\big(d(P,P_i)\big)}{\sum_{i=1}^{M} \sigma\big(d(P,P_i)\big)} \qquad (3)$$

gives a continuous and exact approximation:

$$U(P_i)=F_i \quad \text{for any } i\le M \qquad (4)$$

where $d(P,P_i)$ is the (Euclidean) distance of the points P and P_i and the *positive* "weight function" $\sigma:R\to R^+$ satisfy

$$\lim_{d\to 0+} \sigma(d) = +\infty \quad \text{and} \quad \lim_{d\to+\infty} \sigma(d) = 0+ \,. \qquad (5)$$

(Roughly speaking: $U(P)$ is a weighted arithmetic mean of the measured values F_i with weights, which are "inverses" of the distances of the points P_i from the point P: the more closer is P_i to P, the greater weight of F has in (3).)
Theoretical and practical experiences (see eg. [15], [17]) suggest σ to be chosen to

$$\sigma(d) = d^{-\alpha}\cdot e^{-\lambda d} \qquad (6)$$

for some "approprite" $\alpha,\lambda \geq 1$, usually $1 \leq \alpha,\lambda \leq 2$ are satisfactory in the practice. (This problem is discussed in detail e.g. in [14], [15], [16] and [17].)
In our present calculations we used the values $\alpha=\lambda=1$.

The approximating function U(P) of Shepard' method is drawn in *Figure 4*, detailed numeric values can be found in [19].

The main *advantage* of Shepard's method is the simplicity of the formula (3), which makes both theoretical investigations and practical computations extreme easy. Further, the measuring points P_1 , P_2 , ... , $P_M \in R^n$ can be chosen totally arbitrarily, which may be a great help in empirical measurings.

However, an important *disadvantage* of this method is that σ and so *U* are sensitive on the *measurement units*, MPa or kPa in our case. Though *U* is always continuous and the formula (4) is valid for any σ which satisfies (5), the "shape" of *U* is the best when the distribution of the data points P_i is "nearly" uniform in a region of R^n (see [17], [18]). To improve our approximation we turned the data to kPa in *Table 1*.

Second: larger datasets slower (3) down highly, even for $M \approx 150$ computers run for some minutes. The first idea for managing this problem is to deal only with the data points P_i closest to P . In our example with aqueous glycerol solutions we used 4×4 data points (along pressure and concentration) surrounding the requested approximated point. This trick highly fastened the running times. The continuity property of *U* in this variant is discussed in [15] and [16].

Discussion

For the better comparison of the methods considered in this paper, we constructed two more Figures.

In *Figure 5* we displayed the values for different fixed *concentration*, while in *Figure 6* the *pressure* is examined at fixed values. **Iterated** 1-dimensional splines are in *dashed-dotted lines*, **Lénárd's** Hermite-type 2-dimensional spline is in *dashed lines*, and **Shepard's** method is in *dotted lines*.

On these Figures Lénárd's and iterated splines are practically undistinguishable. It seems that Shepard works worse than the other two methods. We can see from the 3d plot, where the effect of the flattening is evident, from the 2D plot with constant concentration, where estimation in the middle (supposed missing) points is worse (plotted as squares), and from the 2D plot with constant pressure, where again flattening effect is evident.

We can conclude, that though Shepard's method (3), (4) an easy approximation method for general positions of measuring data, it is extremely sensitive for the large and small distances of them. For datasets situated in a rectangular grid (as in *Table 1*), splines methods are more accurate.

The detailed computation results can be seen in [19].

	5.3	**13.3**	**20.2**	**26.6**	**33.3**	**39.9**	**46.6**	**53.3**	**59.9**	**66.6**	**73.3**	**79.9**	**86.6**	**93.3**	**101.3**
0%	34.0	51.6	60.1	66.4	71.6	75.9	79.6	82.9	85.9	88.7	91.2	93.5	95.7	97.7	100.0
10%	34.4	52.1	60.7	67.0	72.3	76.6	80.3	83.7	86.7	89.5	92.0	94.3	96.6	98.6	100.9
20%	34.9	52.7	61.3	67.7	73.0	77.3	81.1	84.4	87.5	90.3	92.9	95.2	97.4	99.5	101.8
30%	35.5	53.4	62.1	68.6	73.8	78.2	82.0	85.3	88.4	91.3	93.8	96.2	98.4	100.4	102.8
40%	36.5	54.4	63.1	69.5	74.9	79.3	83.1	86.4	89.5	92.4	95.0	97.3	99.6	101.7	104.0
50%	37.5	55.7	64.5	71.1	76.4	80.9	84.8	88.2	91.3	94.2	96.8	99.2	101.5	103.6	106.0
60%	39.5	58.0	66.9	73.5	79.0	83.5	87.4	90.9	94.1	97.0	99.7	102.1	104.4	106.0	109.0
70%	43.0	61.7	70.8	77.6	83.1	87.7	91.7	95.2	98.4	101.4	104.1	106.6	109.0	111.1	113.6
80%	49.1	68.2	77.4	84.3	90.0	94.6	98.7	102.3	105.6	108.7	111.4	113.9	116.3	118.5	121.0
90%	59.5	80.2	90.3	97.7	103.9	109.1	113.5	117.4	121.0	124.4	127.4	130.2	132.8	135.2	138.0

Table 1 The measured boiling temperature data of aqueous glycerol solutions in Celsius grades, depending from the pressure (kPa, horizontal) and the concentration (%, vertical) as in [6,Table 44].

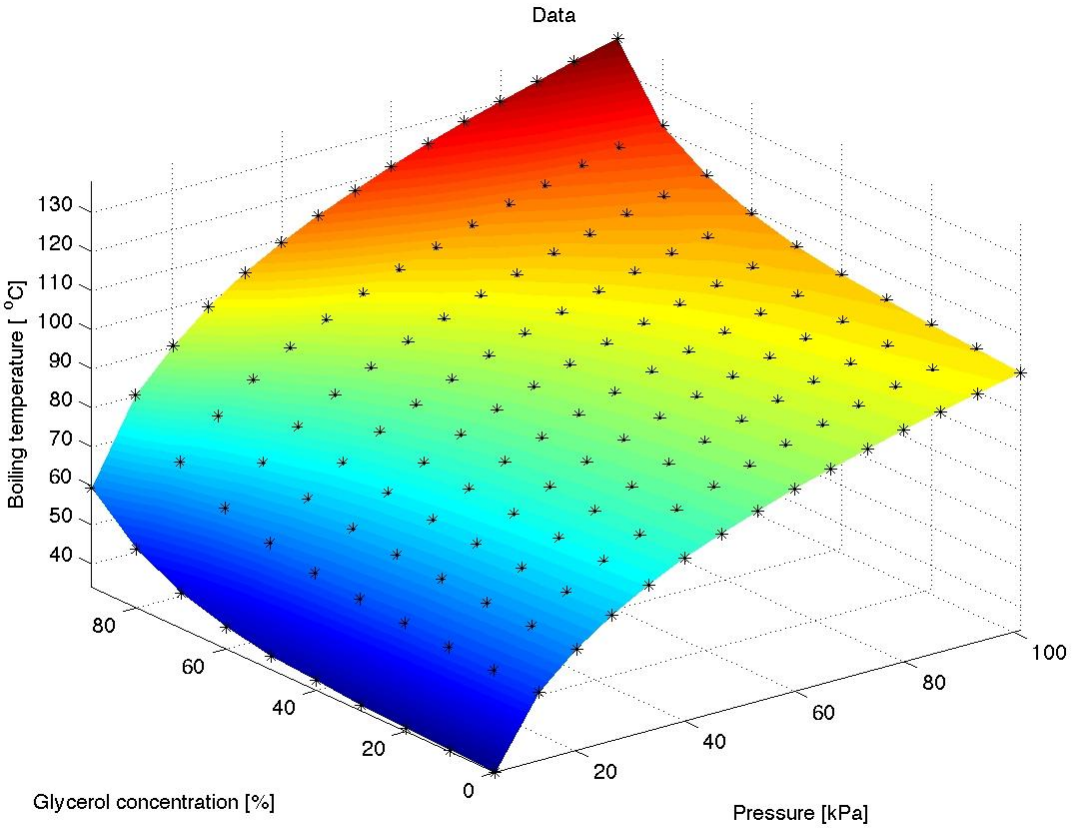

Figure 1 The original dataset from Table 1

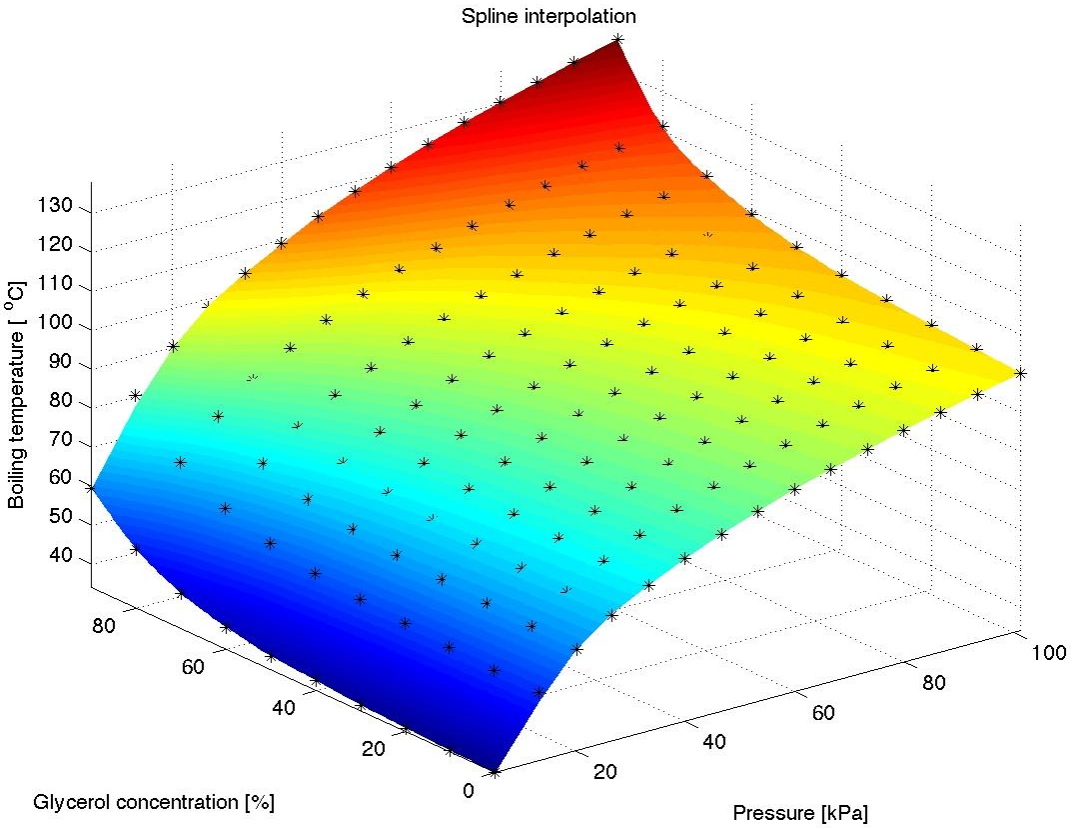

Figure 2 Iterated 1 dimensional splines

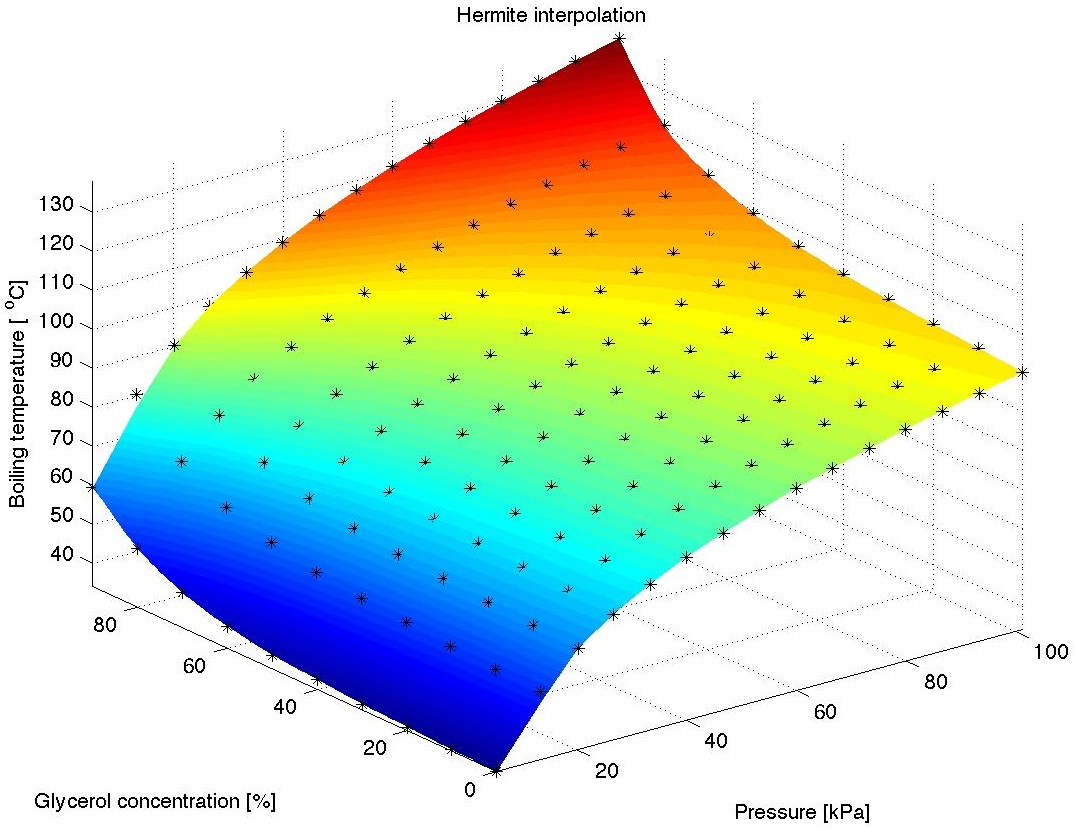

Figure 3 Lénárd's Hermite-type interpolation

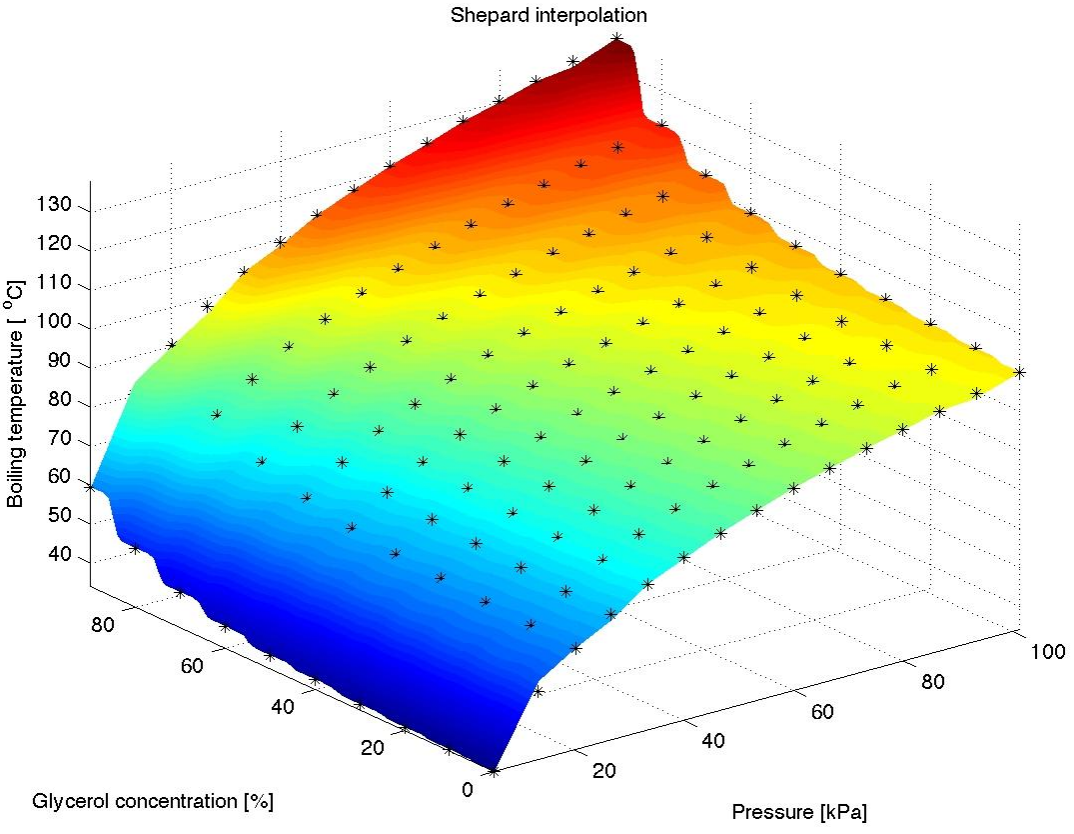

Figure 4 Shepard's method

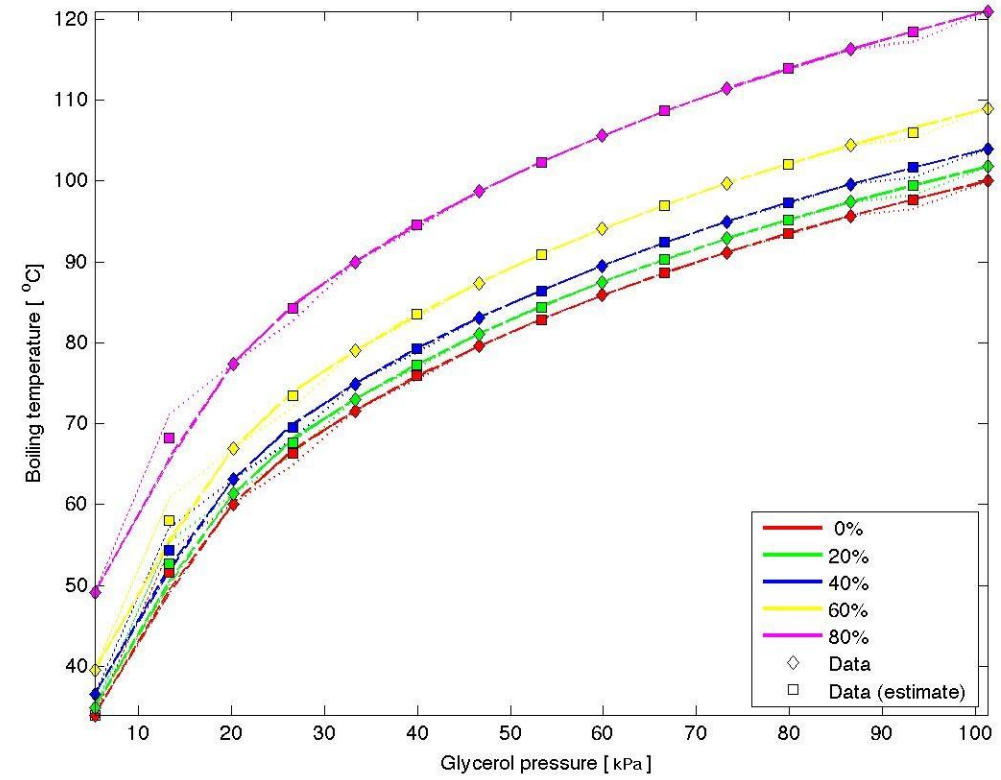

Figure 5 Plots per concentration

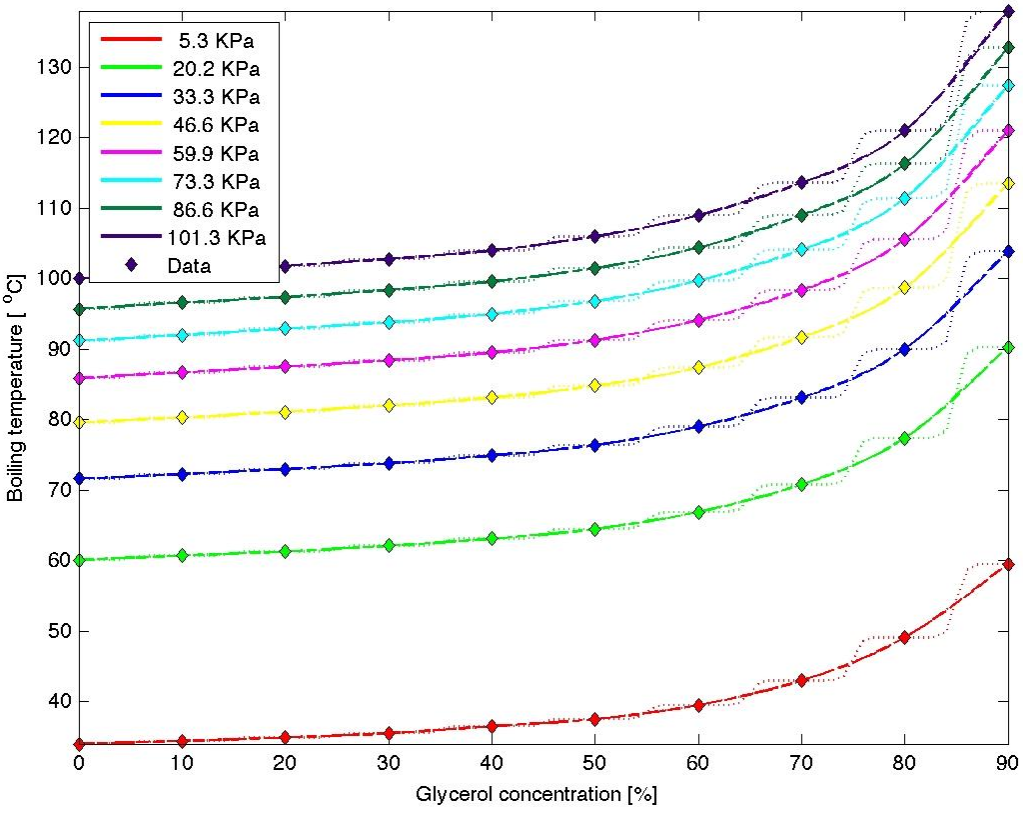

Figure 6 Plots per pressure

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19. *Table 2 : Appendix to the present paper:* http://math.uni-pannon.hu/~szalkai/HJIC-16-Table2-150110.xls