

MATHEMATIC EVALUATION OF THE MICELLAR CRITICAL CONCENTRATION CORRELATED TO SOME ALIMENTARY ADDITIVE PARAMETERS

C. Rujescu, Cristina Tuchilă, C. Jianu, Ileana Negrea, I. Jianu

Faculty of Food Processing Technology, Banat's University of Agricultural Sciences and Veterinary Medicine, Calea Aradului 119, RO-300645, Timișoara

Abstract

This work proposes to mathematically solve (express) a modality of exactly quantifying the σ - CCM coordinates for a general given case, as an integrant part of the preoccupations of the discipline Alimentary Additives, which intends to subsequently correlate these values with doses of additivation daily admitted or maximum recommended by the alimentary Codex for structures of alimentary additivation with superficial-active properties. The proposed and in the current practice generally accepted graphical methods offer preliminary guiding dates which also imply imperfections because of the large family of straight lines to the graphic of the function $\sigma = f(\text{conc.})$, without being able to exactly specify the position (coordinates) of the real point. The graphic method does not return a unique point, but an infinity of points dependent on the way the straight lines to the variation curve $\sigma = f(\text{conc.})$ is graphically constructed.

Key words: *function of the power, micellar critical concentration, derivatised PEG, superficial tension*

Introduction

The micellar critical concentration (MCC) represents a basis colloidal characteristic (parameter) in the theoretical and practical determination of the superficial-active structures. Correlated with the superficial tension (σ) it forms a couple of colloidal defining properties which can offer structure - properties correlations within a scale ruled by the HLB indices (Pedersen, 1967).

MCC is mainly the value to which the separation interface of two phases in a colloidal system macromolecular saturated with tension-

active more or less “loose packed” structures, according to their spatial geometry, ensure the beginning of association in spherical micelles, and determines “violent” modifications of many properties of the solution to be underlined by the inflections of some functions $\sigma = f(\text{conc.})$ (fig. 1).

The establishment with maximum precision of the inflection point coordinates by the graphic method (the intersection of straight lines to the two branches of the variation curve) is disputable, and can be mathematically explained (fig. 2) (Cret, 2000).

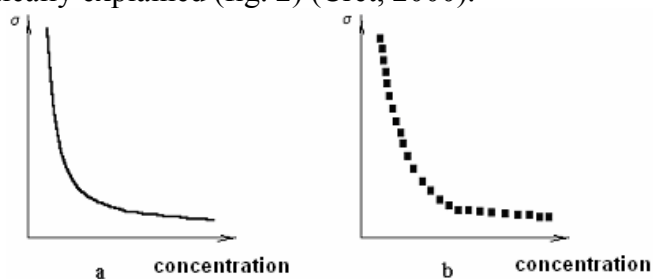


Fig. 1. The dependence of the superficial tension on the concentration
a) Theoretical; b) Experimental

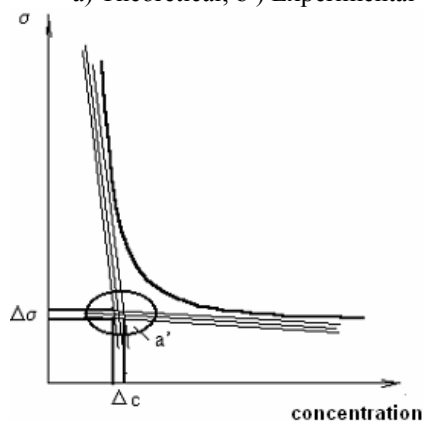


Fig. 2. Possibilities of graphical representation of family of the straight lines to the variation curve $\sigma = f(c)$

From fig. 2 we can see that in such cases one cannot speak about a point but about a zone of maximum probability (a') defined by $(\Delta\sigma)$, respectively (Δc) , where this point exists. The equations of all straight lines which can be drawn too the graphic of the function $\sigma = f(\text{conc.})$ (this has the form $y = ax^{-b}$) are given by the following relations:

$$y = y_0 + m(x - x_0)$$

where: $m = (-ab)x_0^{-b-1}$, and (x_0, y_0) is a variable point, situated on the graphic of the function. It is therefore clear that there is infinity of straight lines (as there is an infinity of x_0 values). These straight lines are not parallel because the gradient does not take different values for each particular case, that is why we have an infinity of intersection points which could be falsely mistaken for the searches critical point.

The work proposes to give a mathematic solution for the exact quantification of the coordinates σ – MCC for a given case.

Experimental

Polyethylene glycol ($n = 9$) „homogeneous” bi-derived with a benzoic radical (lab of the discipline The Technology of Alimentary Additives USAB Timișoara) in fresh bi-distilled water were used. The stalagmometric method described in STAS 6118-5 with subsequently ISO modifications was used for measure superficial tension (Jianu, in press).

Results and Discussions

In figure 3 a graphic representation, which corresponds to some experimental dates representing the number of drops as a function of the concentration of superficial-active solution are presented. It had experimentally noticed that the dependence is the form:

$$y = a \cdot x^{-b}; a, b > 0$$

If we hypothetically split the graphic into two part, a superior and an inferior one, could be notice that in the superior part there is a much higher variation of the expression $f(x_i)$. The opposite phenomenon appears in the inferior part, when a high variation of the x_i factors imply little effects upon $f(x_i)$.

We propose the determination of the point where there is equilibrium. So it could be written:

$$|y(x) - y(x_0)| = |x - x_0|$$

for $x \rightarrow x_0$, $x < x_0$, or:

$$\lim_{\substack{x \rightarrow x_0 \\ x; x_0}} \frac{y(x) - y(x_0)}{x - x_0} = -1.$$

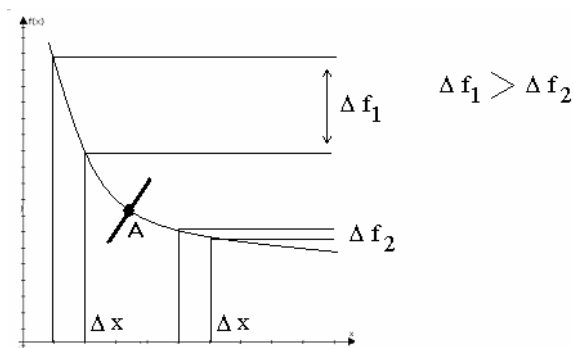


Fig. 3. The dependence of the number of superficial-active concentrated solution drops

Mathematically we must determine the point $A(x_0, y_0)$ so that: $y'(x_0) = -1$. We have:

$$y'(x) = (-ab) \cdot x^{-b-1}$$

$$y'(x_0) = (-ab) \cdot x_0^{-b-1} = -1$$

So:

$$x_0^{-b-1} = \frac{1}{ab} \Rightarrow x_0^{-b-1} = (ab)^{-1}$$

and:

$$x_0 = (ab)^{\frac{1}{b+1}} \quad (1)$$

from here results:

$$y_0 = a \cdot x_0^{-b}$$

from which:

$$y_0 = \frac{a}{(ab)^{\frac{b}{b+1}}} \quad (2)$$

In Table 1 are given the experimental results noticed when studying the dependency of the number of drops on the concentration

of polyethylene glycol (n = 9) „homogenous” di-benzoilated at: 20°C, 30°C, 50°C.

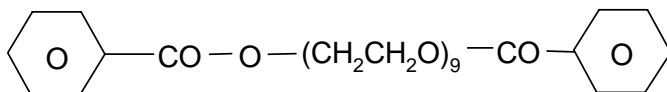


Table 1. Experimental dependence of the number of drops on the concentration of polyethylene glycol

Concentration (g/100)	20°C	30°	50°
	No. of water drops		
$10 \cdot 10^{-1}$	40.18	43.56	49.18
$5 \cdot 10^{-1}$	41.39	44.19	49.98
$2.5 \cdot 10^{-1}$	43.24	45.51	51.68
$1.25 \cdot 10^{-1}$	44.77	46.91	52.43
$6.25 \cdot 10^{-2}$	46.62	49.18	54.45
$3.125 \cdot 10^{-2}$	50.14	50.82	55.44
$1.56 \cdot 10^{-2}$	53.39	53.49	57.63
$7.81 \cdot 10^{-3}$	60.54	59.78	60.98
$3.91 \cdot 10^{-3}$	63.98	64.87	64.87
$1.95 \cdot 10^{-3}$	70.88	70.91	67.87
$9.76 \cdot 10^{-4}$	71.72	70.65	67.76
$4.88 \cdot 10^{-4}$	73.09	70.25	68.24
$2.44 \cdot 10^{-4}$	74.25	70.04	69.18

After graphically representing the three sets of data we notice that the power function:

$$y = a \cdot x^{-b} \quad (3)$$

respects most closely the studied phenomenon.

This is the conclusion reached after analyzing the correlation coefficients for different types of regression functions used in practice. So, at 20°C the following values were obtained:

- The linear function, $r = 0.413$
- The logarithmic function, $r = 0.965$
- The IInd grade function, $r = 0.635$
- The IIIrd grade function, $r = 0.785$
- The exponential function, $r = 0.466$
- The logistic function, $r = 0.466$
- The power function, $r = 0.972$

Mathematic Evaluation of the Micellar Critical Concentration Correlated to Some Alimentary Additive Parameters

We notice that the highest value of the r coefficient corresponds to the power function. Similar results regarding the dimension of the r coefficient have been obtained for all series of experimental dates, a detail which shows that the power function is the most suited.

The following expressions were computed:

$$y = 38.6961 \cdot x^{-0.0852} \quad \text{at } 20^{\circ}\text{C} \quad (4)$$

$$y = 41.7393 \cdot x^{-0.0704} \quad \text{at } 30^{\circ}\text{C} \quad (5)$$

$$y = 48.3976 \cdot x^{-0.0467} \quad \text{at } 50^{\circ}\text{C} \quad (6)$$

The corresponding graphical representations are the ones in the figure 4.

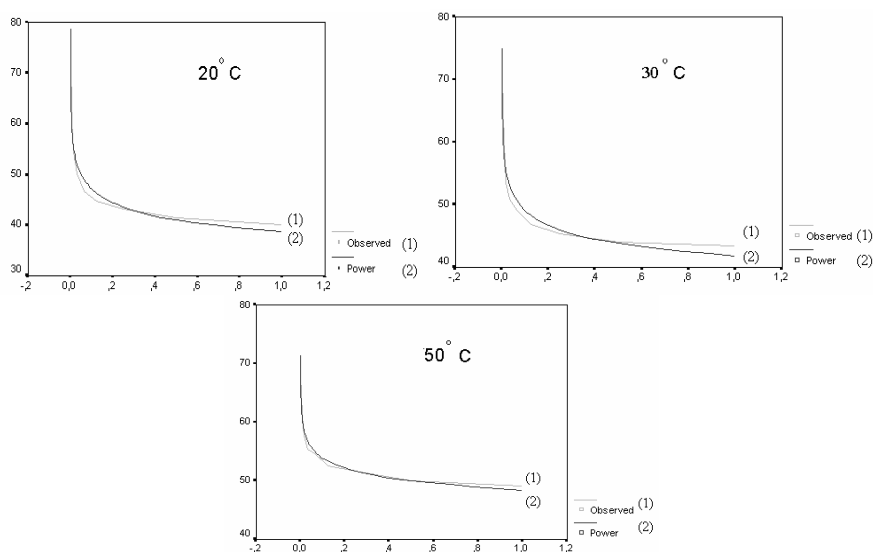


Fig 4. The variation curves for the superficial tension on the concentration at 20°C, 30°C, 50°C for the “homogenous” polyethylene glycol (n=9) bi-derived through benzoilation

Applying (1), (2) for the expressions of the functions (4), (5), (6) were obtained the values for superficial tension and micellar critical concentration, at the three used temperatures. These values are presented in table 2.

Table 2. The values of superficial tension and micellar critical concentration at 20°C, 30°C and 50°C

Temperature (°C)	Superficial tension (dyn/cm)	Micellar critical concentration (mol/l · 10)
20	3.00	42.50
30	2.73	44.81
50	2.17	50.19

The dependence of MCC on superficial tension at studied temperatures is shown in the fig. 5. Could be notice that the value of the correlation coefficient is $r = -0.99962$ so in the very vicinity of the extreme $r_{\min} = -1$, which indicates a powerful linear correlation: the little values of the superficial tension correspond to high MCC values and the other way around.

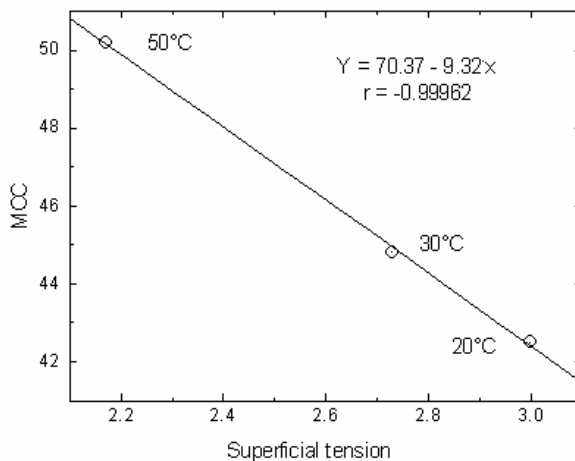


Fig. 5. The equation of the regression line and of the correlation coefficient for dependence of MCC on superficial tension at 20°C, 30°C and 50°C

Conclusions

The hypothesis, which has determined the present approach, has confirmed the justness and the theoretical, practical and technological use. There are some supplementary things to be mentioned:

Mathematic Evaluation of the Micellar Critical Concentration Correlated to Some Alimentary Additive Parameters

1. Knowing the exact micellar critical concentration (MCC) of the alimentary additive structure allows the rigorous correlation with the international accepted values for the maximum additivation doses.
2. Knowing the exact MCC also implies benefic economic effects related to the specific consumption of additives during a certain alimentary processing.
3. Knowing the exact MCC also assures the minimum demand of alimentary additive in order to obtain the colloidal effect imposed by the studied technology.

References

- Creț, F., Rujescu, C., Rotariu, L., Boldea, M., Ivan, M. (2000). *Elemente de matematici speciale. Teorie și aplicații*. Ed. Mirton
- Jianu, C. și colab., unpublished data, or in press
- Pedersen, C.J. (1967). *J. Amer. Chem. Soc.*, 89(9), 7017, 1967