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Sucrose Crystallization: Modeling of Thermodynamic Equilibrium in Impure Aqueous Solutions

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ABSTRACT

Crystallization is an important process in industrial operations. In sugar manufacturing, crystallization is a crucial step that determines the quality of the final product, which requires control of its fundamental parameters especially thermodynamic parameters. In fact, to study the crystallization of sucrose, it is extremely important to know the sucrose solubility, which reflects a thermodynamic equilibrium, and how it can vary in the presence of non-sucrose (impurities). Indeed, in crystallization, solubility is of fundamental importance in the definition of supersaturation which is the driving force of crystallization. In this study, the sucrose solubility has been modeled as a function of sucrose concentration, mass percentage of glucose and fructose applying a full factorial design. The validation of the developed model was verified by additional batch experiments. The results confirm that the proposal model provided a satisfactory fit to the experimental data. The results also show the decrease in the sucrose solubility with the increase in the mass percentage of glucose and fructose.

Keywords*—thermodynamic equilibrium; crystallization; sucrose; fructose; glucose; experimental design.*

I. INTRODUCTION

Crystallization is a separation and purification process frequently employed in the industry, particularly in the sugar industry [1]. Two crucial parameters in crystallization are temperature and solvent. The solvent affects the solubility of the crystals, which constitutes the basis for any crystallization process [2-5]. The solubility concentration and its dependence on temperature determine the yield of the process and the generation of supersaturation (driving force of crystallization) [6, 7]. Solubility reflects a thermodynamic equilibrium in which the chemical potential of the solute is equal to the chemical potential of the solid phase [8]. To be able to control a crystallization process we need to know the solubility of the different solid forms and how they are related to the solvent and temperature [9]. In the sugar industries the impurities or non-sucrose found in the sugar juice affect the sucrose solubility which influences the sucrose crystallization and consequently the quality of the sucrose produced will be impacted [10-12]. So to deal with the problems related to crystallization process, it is extremely important to master the sucrose solubility in the presence of impurities. For this, in this study, the sucrose solubility will be modeled as a function of sucrose concentration and in presence of glucose and fructose as impurities using the experimental design method especially the full factorial design.

II. EXPERIMENTAL SECTION

Sucrose, glucose and fructose employed are "of analytical" quality to avoid any other impurities which may influence the measurements. Distilled water is used as solvent. The experiments were conducted in a jacketed reactor with a mechanical stirrer. A cryothermostat has been used for temperature control. The temperature in the reactor is controlled by a digital thermometer. The cooling is carried out by a cryothermostat and the determination of the solubility is performed using the spectrophotometric method [10].

III. RESULTS AND DISCUSSIONS

A method to illustrate the influence of impurities on the sucrose solubility is to follow the deviation from the thermodynamic equilibrium, in other words the difference between the solubility in a pure system and that in the case of the presence of impurities. In this study and in order to elucidate the effect of glucose and fructose additives on the sucrose solubility in water, this deviation has been modeled as a function of sucrose concentration, mass percentage of glucose and mass percentage of fructose using the experimental design method especially the full factorial design [13]. The experimental design is a powerful method of experimentation which presents a complex system in the form of mathematical equations. The experimental design helps to study the effects caused by independent factors and their interactions [14]. If we call n the number of variables to be tested, in order to measure the effect of all the variables combinations when each variable is tested at a high and a low level, 2^n experiments will be needed [15]. Two levels for each factor have been selected according to the average composition of the sugarcane [16]. The natural values of each factor and their respective levels are presented in Table I. The different experiments performed in this study are shown in Fig.1.

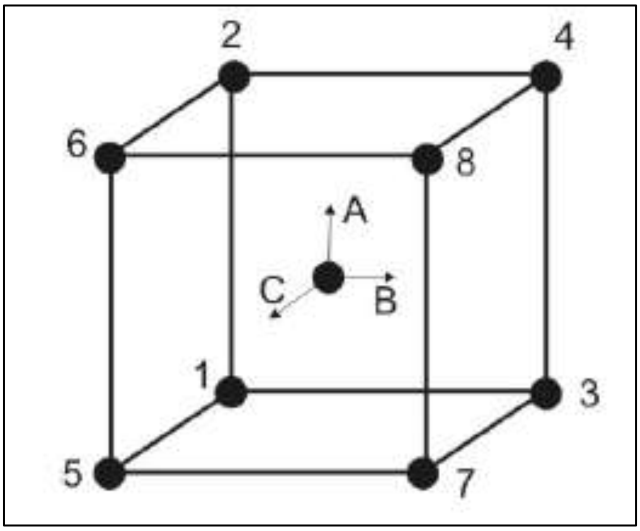


Fig.1. 2^3 full factorial design.

TABLE I. THE EXPERIMENTAL RANGES AND LEVELS OF INDEPENDENT VARIABLES.

Factors	Symbol	Low level (-1)	High level (+1)	Unit
Concentration of sucrose	X_1	220	240	g/100g water
Mass percentage of glucose	X_2	0.05	0.15	% weight
Mass percentage of fructose	X_3	0.05	0.15	% weight

The behavior of the system is explained by the following model:

$$\hat{y} = a_0 + \sum_{i=1}^{k} a_i x_i + \sum_{i=1}^{k}\sum_{j=1}^{k} a_{ij} x_i x_j + \varepsilon \qquad (1)$$

Where $\hat{y}$ is the response (dependent variable), a_0 is the value of fitted response at the center point of design, a_i is the linear effect and $a_{ij}$is the interaction terms. It should be noted that the x_i is the coded value of the i^th^ variable. The coded values were obtained from the following relationship [17-19]:

$$x_i = \frac{X_i - X_0}{\Delta X_i} \qquad (2)$$

With: $X_0 = (X_{imax} + X_{imin})/2$; $\Delta X_i = (X_{imax} - X_{imin})/2$

Where x_i is the coded value of i^{th} variable, X_i is the encoded value of i^{th} variable, $X_0$is the value of X_i at the center point of the investigation domain and ΔX_i is the step size. Here, X_{imax} and X_{imin} represent the maximum and the minimum level of factor i in natural unit, respectively. According to full experimental design, 2^3 experiments were conducted and the values of the deviation from the equilibrium (response y) were tabulated (see Table II).

Using Minitab software, the experimental data are analyzed and the following polynomial equation in coded form was established to explain the effect of sucrose concentration, mass percentage of glucose and mass percentage of fructose on the thermodynamic equilibrium in the sucrose crystallization in aqueous solutions.

$$\hat{y} = 15.62 + 1.358x_1 + 3.169x_2 + 7.979x_3 + 0.4769x_1x_2 + 0.6886x_1x_3 + 0.9771x_2x_3 \qquad (3)$$

In order to verify the validity of the developed model, several additional batch experiments were carried out in the experimental area of each factor, and each experimental response was compared with the predicted one (see Table III). As Table III shows, the proposed model provided a satisfactory fit to the additional experimental data.

TABLE II. EXPERIMENTAL DESIGN MATRIX.

Experiment	**X_1**	**X_2**	**X_3**	**y (g)**
1	220	0.05	0.05	5.535
2	240	0.05	0.05	5.373
3	240	0.15	0.05	11.257
4	220	0.05	0.15	17.615
5	240	0.15	0.15	30
6	220	0.15	0.05	8.417
7	220	0.15	0.15	25.5
8	240	0.05	0.15	21.302

TABLE III. MODEL VALIDATION.

Additional Experiment	**Observed, y (g)**	**Estimated, ŷ (g)**	**Error**
(0,0,0)	15.525	15.620	0.005
(0.5,0.5,0.5)	22.412	22.408	0.003
(-0.5,-0.5,-0.5)	9.91	9.902	0.007

From equation 3 and according to Vavrinecz's equation [20] giving the solubility-temperature dependence, the following model can be deduced to predict the solubility temperature ($T_s, °C$) as a function of sucrose concentration and mass percentages of glucose and fructose.

$$T_s = 43.59 + 5.788\, x_1 + 1.212\, x_2 + 3.538\, x_3 + 0.1625\, x_1x_2 + 0.08750\, x_1x_3 + 0.6625\, x_2x_3 \qquad (4)$$

The values obtained by the model (ŷ predicted) are compared with those of experimental data (y experimental) (Table IV). The goodness of fit of the model was checked by the determination coefficient (R^2). In this case, the value of determination coefficient ($R^2 = 0.999$) indicated that only 0.1% of the total variations were not explained by the regression model (see Fig. 2). To verify the systematic departures from the assumptions that errors are normally distributed and are independent of each other and that the error variances are homogeneous, a diagram of residual values by order was constructed (see Fig. 3). The random distribution of residuals confirms their normality and independence.

TABLE IV. COMPARISON BETWEEN OBSERVED AND PREDICTED RESPONSES.

Runs	**y**	**ŷ**	**Residuals**
1	21.302	21.0226	0.2794
2	5.535	5.2566	0.2784
3	8.417	8.6866	-0.2696
4	25.5	25.2216	0.2784
5	17.615	17.8832	-0.2682
6	11.257	10.9792	0.2778
7	5.373	5.6416	-0.2686
8	30	30.2686	-0.2686

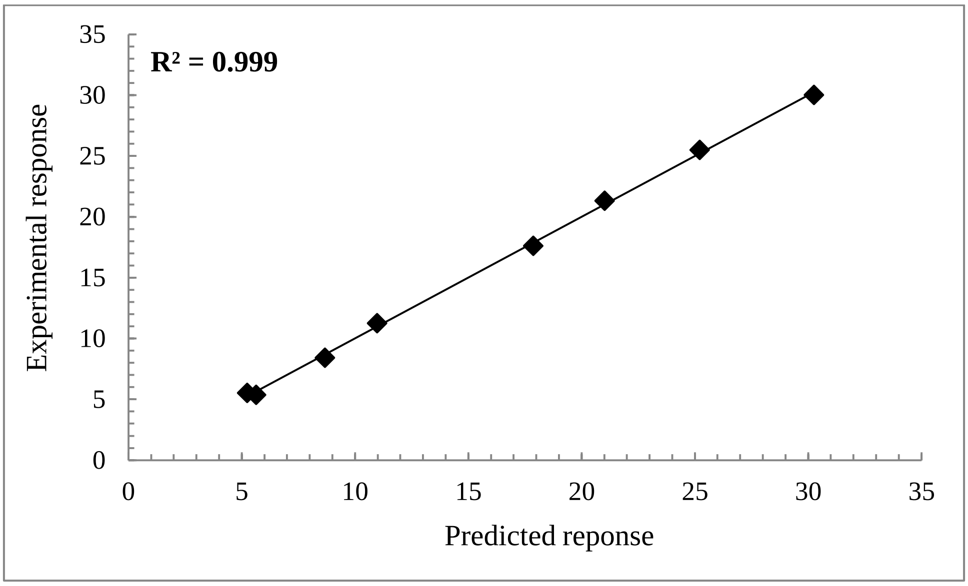


Fig. 2: Comparison of experimental and predicted responses.

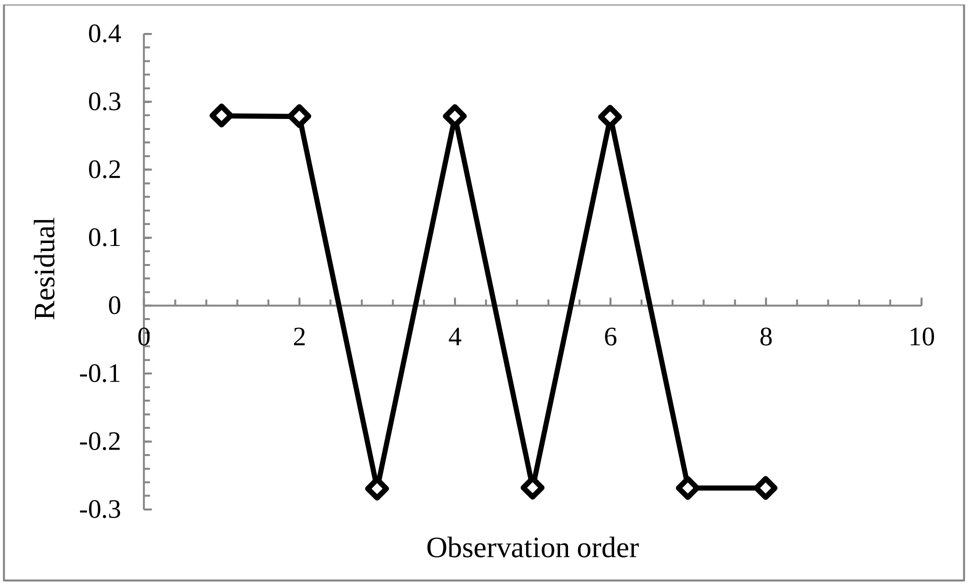
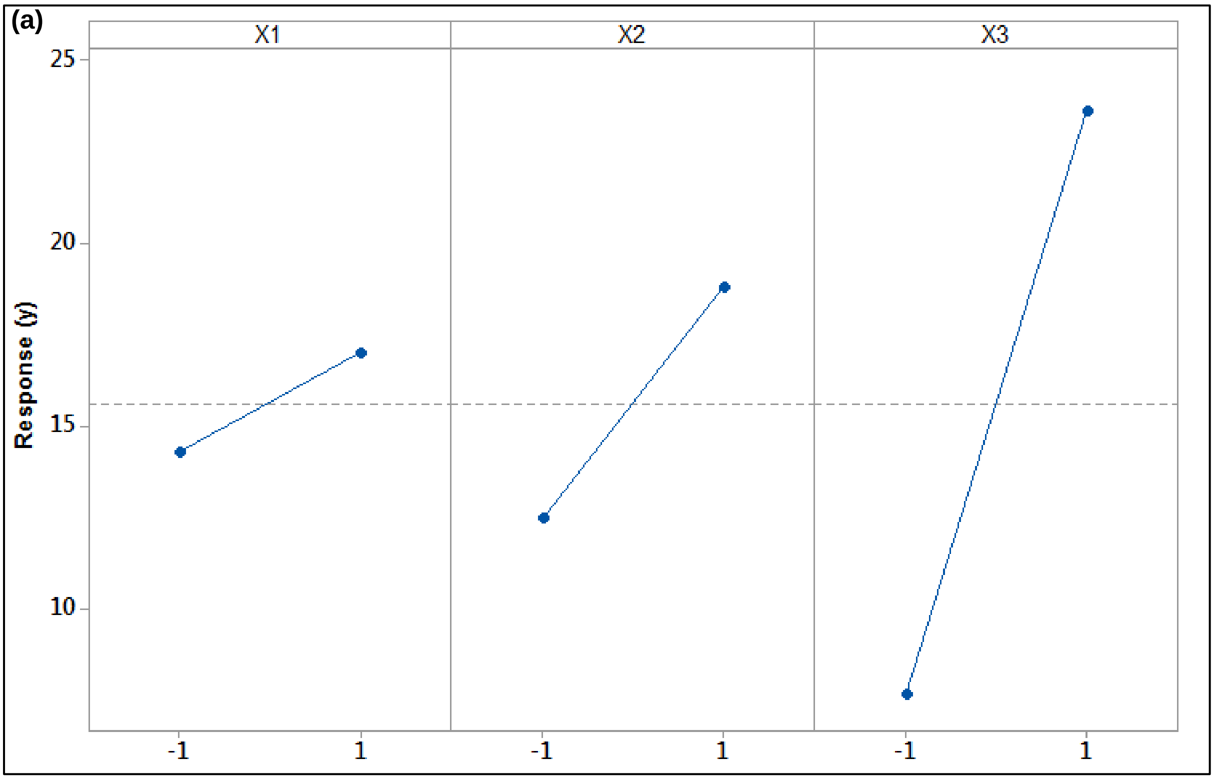


Fig. 3. Residual values according to the order.

To illustrate the effect of sucrose concentration (x_1), mass percentage of glucose (x_2) and mass percentage of fructose (x_3) on the sucrose solubility, the effects diagram and contour plots have been constructed (see Fig. 4 and 5). The results show that the sucrose solubility decreases in the presence of glucose and fructose. This is in good agreement with the results previously published by the authors [10].



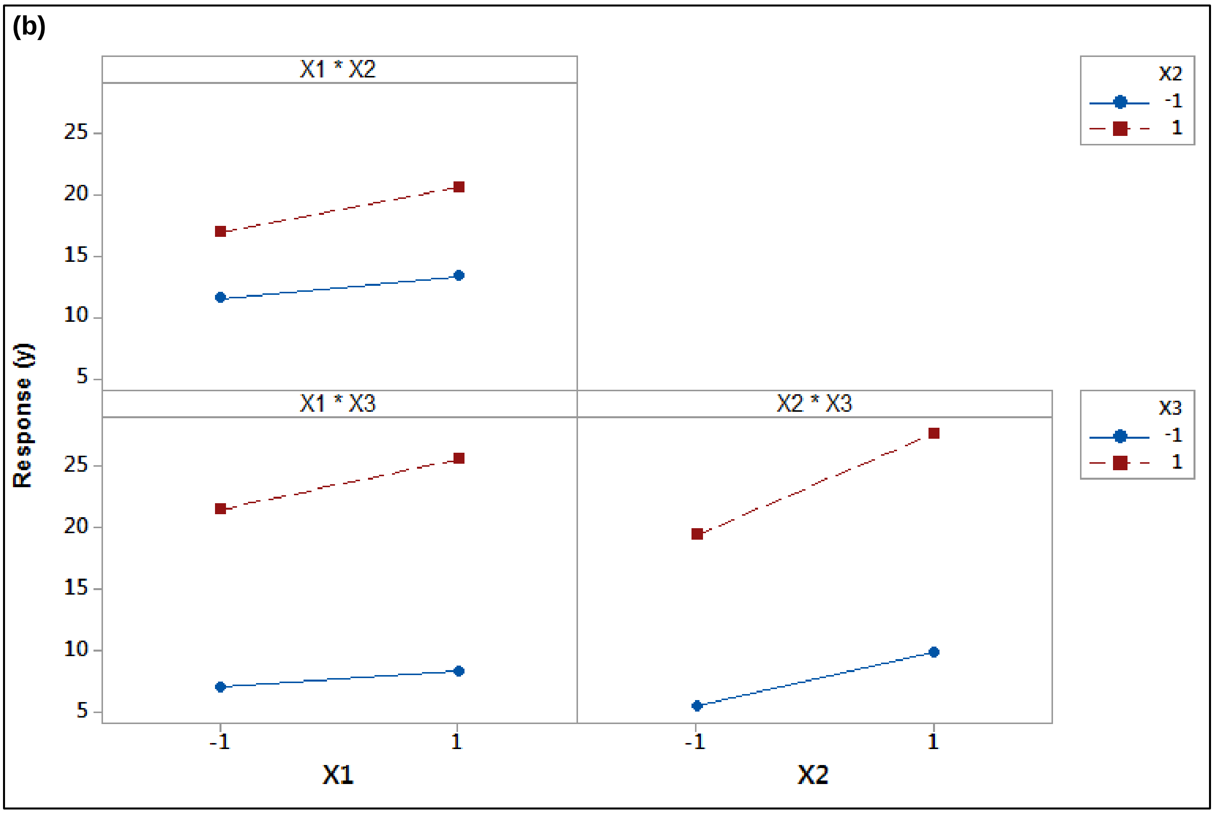
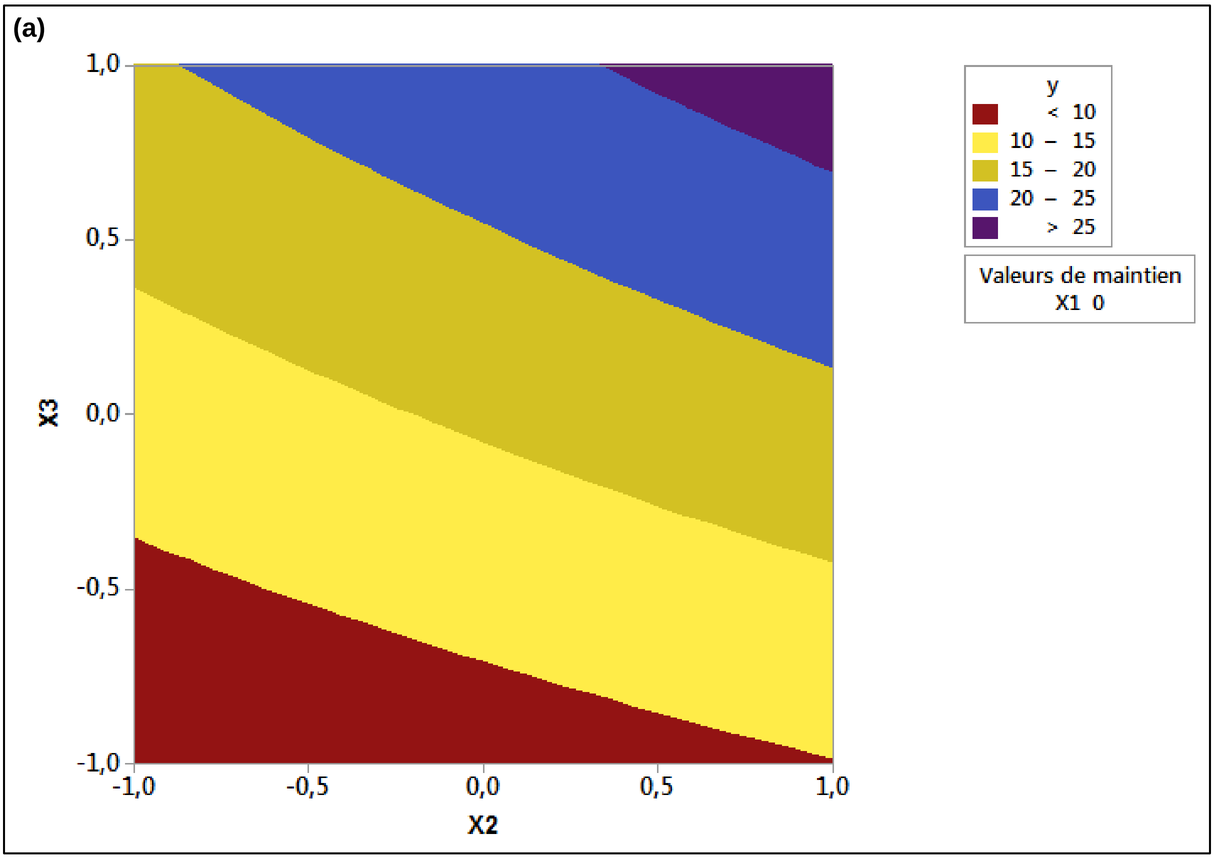


Fig. 4. Effects diagram, (a): main effects of the independent variables, (b) effects of interactions between independent variables.



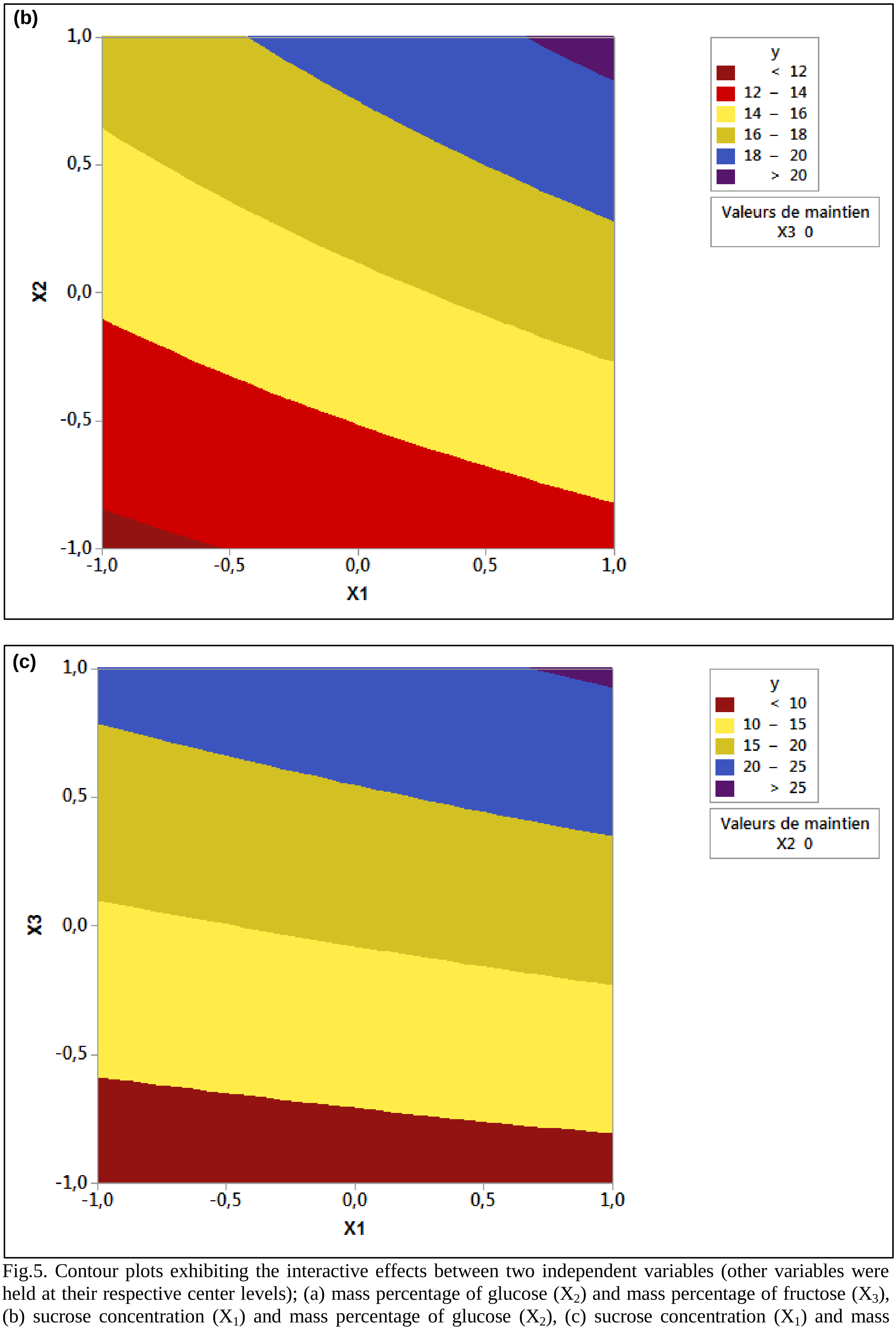


Fig.5. Contour plots exhibiting the interactive effects between two independent variables (other variables were held at their respective center levels); (a) mass percentage of glucose (X_2) and mass percentage of fructose (X_3), (b) sucrose concentration (X_1) and mass percentage of glucose (X_2), (c) sucrose concentration (X_1) and mass percentage of fructose (X_3).

IV. CONCLUSION

In this study, the sucrose solubility (thermodynamic equilibrium) has been modeled as a function of sucrose concentration and mass percentages of glucose and fructose applying the experimental design method. Predicted values obtained using the model equation were in very good agreement with the observed values ($R^2 = 0.999$). The prediction capability of the proposed model was verified by additional batch experiments conducted in the experimental area of each factor. The validation results confirm that the developed model provided a satisfactory fit to the experimental data. The results show that the presence of glucose and fructose in the mixture causes a sucrose solubility decrease.

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