

## Prediction of Wine Foaming

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A procedure for estimating the foam properties of sparkling base wines without specifically measuring foam was developed. This method was based on mathematical equations established between the usual parameters of wine quality control (independent variables of the equations) and the wine foam parameters [foamability (HM), Bikerman coefficient ( $\Sigma$ ), and surface tension (ST)] obtained with the specific equipment (dependent variables of the equations). Ninety-six white wines from the Cava region produced at industrial scale were used to establish these equations. Two predictive equations that could be applied to different types of wine from different origins were obtained: one to predict the foamability (HM) and the other to predict the Bikerman coefficient ( $\Sigma$ ). Moreover, the database of foam parameters of the 96 wines allowed a qualitative assessment of wine foaming values.

**Keywords:** Prediction; foam capacity; physicochemical characteristics; white wine; multiple regression model

### INTRODUCTION

The foam of sparkling wines determines their quality. Some studies have proposed several methods and parameters for determining foam properties in wine-making products (Bikerman, 1938; Edwards et al., 1982; Maujean et al., 1990; Robillard et al., 1993; Gallart et al., 1997). The first automated and computerized equipment, based on the gas sparging method, was the Mosalux (Maujean et al., 1990). Gallart et al. (1997) consider that, with this equipment, the best parameters for characterizing the foam capacities of several wines were foamability (HM) and the Bikerman coefficient ( $\Sigma$ ). Other authors used surface tension (ST) to define foaming of alcoholic beverages or model solutions, because it is related to foam capacity (Maujean et al., 1990; Maeda et al., 1991; Dussaud et al., 1994).

Other studies of foaming in wine-making showed relationships between foam properties and the physicochemical characteristics of grape juices, base wines, or sparkling wines (Maujean et al., 1990; Viaux et al., 1991; Brissonnet et al., 1991, 1993; Robillard et al., 1993; Malvy et al., 1994; Dussaud et al., 1994; Pueyo et al., 1995; Andrés-Lacueva et al., 1996, 1997; López-Barajas et al., 1997).

The aim of this study was to provide an alternative method for determining the foam properties of sparkling base wines, from their relationships to physicochemical characteristics, without the use of Mosalux or tensiometer equipment. This method would be based on mathematical equations established between the foam parameters (dependent variables of the equations) and the

physicochemical characteristics of wine, such as ethanol content, proteins, pH, titratable acidity, and organic acids (independent variables of the equations). As these characteristics are usually determined in juices and wines for quality control, wine-makers could already have information about the foam properties of wine-making products, without any additional measurements. Moreover, the predictive equations could help wine-makers select the most appropriate monovarietal base wines to make blends, which are the raw material for cava (Spanish sparkling wine) (Certified Brand of Origin in Spain). Furthermore, wine-makers often buy wines from other cellars to increase their cava production, and so the application of these equations could easily give them information on which base wines should be selected.

The predictive equations could be applied to different types of wine (cloudy wines and base wines) and to wines from different varieties, years of harvest, and wineries. As there was no qualitative interpretation of foam results (obtained with Mosalux and tensiometer), 96 wines were studied, both to give a wide range of foam capacities and to obtain a database enabling foam values to be assessed. These wines were from the white varieties that were to be used for cava, from four years of harvest and obtained on an industrial scale from 10 wineries in the Cava region. Foam capacity was measured by Mosalux and tensiometer equipment. Physical and chemical parameters that might affect foam were determined.

### MATERIALS AND METHODS

**Samples.** Ninety-six white wines were obtained at industrial scale, from 10 different wineries in the Cava region (66, 8, 2, 2, 2, 4, 1, 3, 2, and 6 from each winery) during four years of harvest (22, 16, 28, and 30 of each year of harvest, respectively).

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These samples were each single-variety wines from white grapes grown in the Cava region (Macabeo, Xarel.lo, Parellada, and Chardonnay) (28, 28, 28, and 6, respectively) and their blends (6).

The different wines were collected at the winery after fermentation (cloudy wines), fining (addition of bentonite, gelatine, etc.), stabilization with cold (4 °C; to eliminate potassium bitartrate), and filtration (filtered wines) (48 of each).

**Analytical Methods.** Foam was measured according to the Mosalux method (Maujean et al., 1990). Following Gallart et al. (1997) and Robillard et al. (1993), the foam parameters chosen were foamability (HM) [maximum height (mm) reached by the foam after CO<sub>2</sub> injection through the glass frit] and the Bikerman coefficient ( $\Sigma$ ) [bubble average lifetime (s) at constant height of foam collar during CO<sub>2</sub> injection]. Surface tension (mN/m) was measured at room temperature (22 ± 1 °C) with a Krüss GmbH K6 tensiometer (Weser, 1980); a correction factor [ratio between theoretical (72 mN/m) and experimental ST of double-distilled water] was applied (to obtain the real surface tension of wine, each experimental result being multiplied by this factor). The tensiometer used was based on the ring method and the surface tension was measured when the ring was pulled out of the surface.

Enological parameters such as pH, titratable acidity (g of tartaric acid/L) and volatile acidity (g of acetic acid/L), ethanol content (% v/v), density (g/L, 20 °C), conductivity (mS/cm), sugars (g of glucose/L), free, combined, and total sulfur dioxide concentrations (mg of SO<sub>2</sub>/L), and absorbances at 280 and 420 nm (ua × 1000) were measured according to OIV methods (1990). The concentration of soluble proteins (mg/L) was determined by using the Bradford method (1976) and total, neutral, and acid polysaccharide contents (mg/L) by the procedure developed by Segarra et al. (1995). Concentrations of organic acids, glucose, fructose, and glycerol (g/L) were measured according to the method of López-Tamames et al. (1996). Analysis of volatile compounds (alcohols and ethyl acetate) (mg/L) was performed by gas chromatography [direct injection of 2  $\mu$ L of sample (containing 4-methyl-2-pentanol as internal standard) into a Seelcosteal Alcohol Carbowax 1500 (4 m × 1/8 cm) column with a 15 cm precolumn; the initial oven temperature was 45 °C for 1 min, the heating rate was 2 °C/min, and the final oven temperature was 80 °C for 45 min; FID detector and injector were both at 180 °C; nitrogen (20 mL/min) was the carrier gas].

All experiments were performed in triplicate except the ST measurements, which were repeated at least five times.

**Statistical Procedures.** Statgraphics 7.0 was used to carry out the statistical data analysis. The three results obtained for each parameter (in the case of the ST, the maximum, the minimum, and the median of the five results) were included on the data matrix, to estimate the analytical variation or experimental error.

Correlation analysis was performed among the three foam parameters [foamability (HM), Bikerman coefficient ( $\Sigma$ ), and surface tension (ST)] of all wines ( $n = 96$ ).

To obtain the predictive empirical equations, multiple linear regression analysis was applied to the physical and chemical characteristics of wines as *independent variables* and to the foam characteristics of the same wines as *dependent variables*. To simplify the predictive equation obtained, the nonsignificant ( $p < 0.05$ ) variables were removed manually, and then the regression was repeated until all of the independent variables were significant. The multiple regression was computed with four-fifths of the total number of samples (data set); the other fifth was used to test the predictive model (test set). This division of the samples was based only on the foamability (HM) of the wines, so that the two groups of samples (data set and test set) had a representative distribution of HM values, but neither the origin of wines (grape variety, winery, and year of harvest) nor their stage of wine-making process was considered.

For each equation with an  $R^2$  coefficient (R-SQ) > 0.6000, an analysis of variance (ANOVA) was performed to examine

the residuals. Only the models with a significant ( $p < 0.05$ )  $F$  ratio were tested. To test the predictive equations, a goodness-of-fit analysis was performed between the predicted values and the experimental values of the test set, used so only to check the equations. When the correlation coefficient of this regression was significant ( $p < 0.05$ ), the prediction was considered to be satisfactory. In addition, the percentage of predicted samples was evaluated. It was accepted that a wine was correctly predicted when the variation between the foam parameter predicted and its experimental value (Mosalux or tensiometer measurements) was lower than the analytical variation ( $\pm 2\sigma$ ). Moreover, for each foam parameter, to check the predictive equations, the root mean standard error of prediction (RMSEP) was also calculated, using the one-fifth part of the samples (test set) as follows (Martens and Naes, 1989):

$$\text{RMSEP} = \sqrt{\frac{\sum (X_{\text{mod}} - X_{\text{exp}})^2}{n}} \quad (1)$$

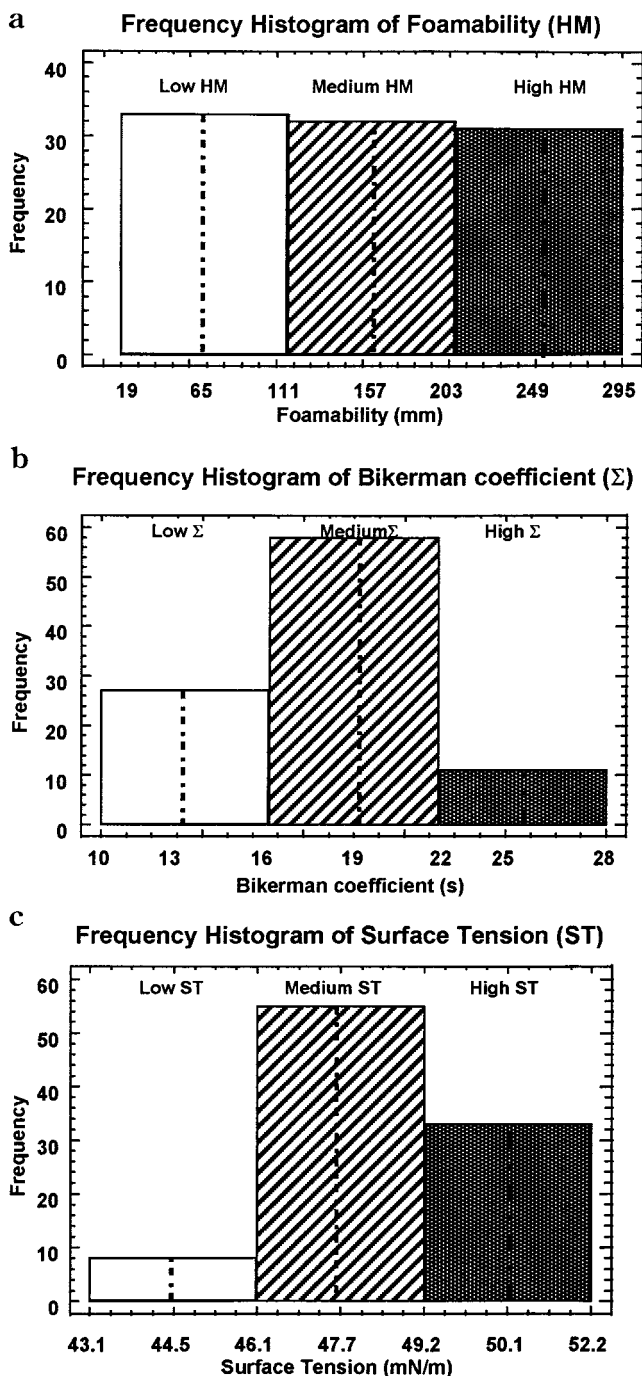
In eq 1  $X_{\text{mod}}$  = value of the foam parameter (HM,  $\Sigma$ , or ST) predicted by the model (predictive equation),  $X_{\text{exp}}$  = value of the foam parameter (HM,  $\Sigma$ , or ST) obtained experimentally, with the Mosalux or the tensiometer, and  $n$  = number of samples used in model testing.

## RESULTS AND DISCUSSION

Figure 1, parts a, b, and c, shows the frequency histograms of the three foam parameters of the 96 wines: foamability (HM), Bikerman coefficient ( $\Sigma$ ), and surface tension (ST), respectively. Three categories in each foam parameter were established according to the limits of the respective histogram: high, medium, and low (Figure 1); using the average value of each category, these categories were also divided into two subcategories. The wines were then classified in six levels of HM,  $\Sigma$ , and ST. Therefore, the database of foam parameters of the 96 wines enabled wine foaming values to be assessed qualitatively. This is the first time that a qualitative interpretation of the quantitative analysis of foam properties is given.

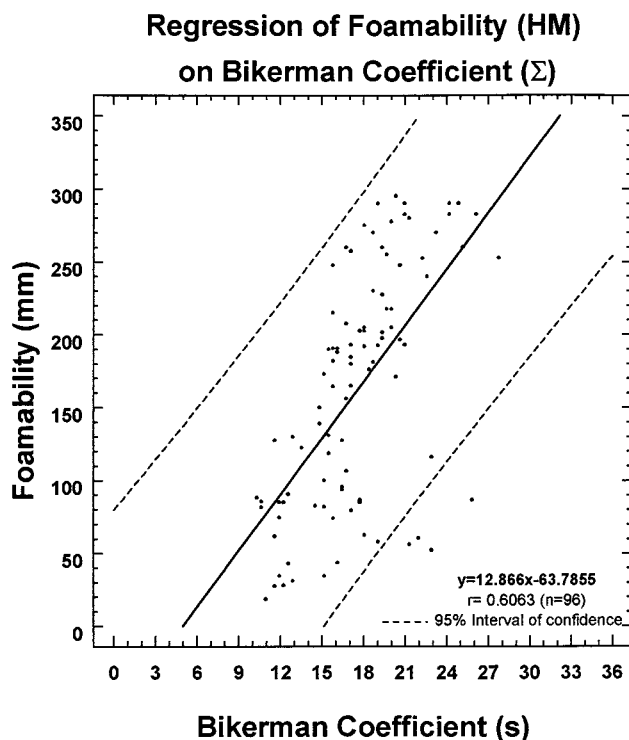
Foamability (HM) and Bikerman coefficient ( $\Sigma$ ) of wines were positively correlated ( $r = 0.6063$ ;  $p < 0.0001$ ). Therefore, wines with high foamability had a long bubble lifetime (Figure 2).

These two foam parameters (HM and  $\Sigma$ ) of all the wines ( $n = 96$ ) could be predicted (Table 1) from their physicochemical characteristics, using mathematical equations (Table 2). However, the prediction of the surface tension (ST) of these wines was not attempted, because the ST equation had an R-SQ < 0.6000 (Table 1). The test of the HM and  $\Sigma$  equations was satisfactory, because the correlation coefficients between the model and the respective experimental foam parameters were significant (Table 1), and, also, the RMSEP values of the HM and  $\Sigma$  equations (35 mm and 4 s, respectively; Table 1) were acceptable. The predictive models allowed the classification of wines, according to the established categories of foam properties [foamability (Figure 1a) and Bikerman coefficient (Figure 1b)], because the RMSEP values of these models were low enough. The percentage of wines that were correctly predicted was also satisfactory (Table 1). In addition, most of the parameters of these equations were provided by simple and/or usual determinations in wine cellars (Table 2). Therefore, these empirical equations could be rapidly applied and give information about foaming of wines with no additional measurement.



**Figure 1.** Frequency histograms of the three foam parameters [foamability, HM (a); Bikerman coefficient,  $\Sigma$  (b); and surface tension, ST (c)] of all wines ( $n = 96$ ).

These relationships were established with a highly heterogeneous group of wines, from different grape varieties, years of harvest, and wineries and at different stages of the wine-making process (cloudy wines and filtered wines). Therefore, the equations were able to predict different levels of HM and  $\Sigma$  and in wines from several origins. However, to obtain predictive equations for each foam parameter and a better prediction (with higher R-SQ and lower RMSEP values), we performed multiple regression with more homogeneous groups of wines. To that end, we grouped the samples according to their qualitative characteristics (winery, type of wine, and grape variety) and then several predictive equations were established for each group of wine (Tables 3 and 4).



**Figure 2.** Relationship between foamability (HM) and Bikerman coefficient ( $\Sigma$ ) of all wines ( $n = 96$ ).

**Table 1. Results of Multiple Regression Models of Foam Parameters [Foamability (HM), Bikerman Coefficient ( $\Sigma$ ), and Surface Tension (ST)] of All Wines ( $n = 96$ )**

	all wines ( $n = 96 \times 3$ ) data set: 76 wines validation set: 20 wines	foamability HM (mm)	Bikerman coeff $\Sigma$ (s)	surface tension ST (mN/M)
prediction	R-SQ <sup>a</sup>	0.6971	0.6423	0.5699
	no. of parameters of the equation <sup>b</sup>	12	10	13
validation	regr (mod-exp) <sup>c</sup>	$r = 0.8982$ ; $p < 0.0001$	$r = 0.4291$ ; $p = 0.0006$	
	% of prediction <sup>d</sup>	65	65	
	RMSEP <sup>e</sup>	35	4	

<sup>a</sup> R-square (R-SQ). <sup>b</sup> Number of parameters of the equation. <sup>c</sup> Regression coefficient ( $r$ ) and significance level ( $p$ ) of the relation between the model and the experimental values of the foam parameter. <sup>d</sup> Percentage of well-predicted samples. <sup>e</sup> Root mean standard error of prediction. <sup>f</sup> The three results obtained for every parameter in each wine were considered.

**Predictive Equations Obtained with Wines from the Same Winery.** Two predictive equations were established (Table 3) for the wines from the winery that had the highest number of samples ( $n = 66$ ): one to predict foamability (HM) and the other to predict surface tension (ST) (Table 4). Although the RMSEP values were similar, the HM equation was better than the HM equation obtained with all of the samples, because it had a higher R-SQ, a better relationship between model HM and experimental HM, and a lower number of parameters, which makes the equation easier to apply (Table 3 and Figure 3). The ST equation had a satisfactory RMSEP (Table 3) when compared to the ST values of the samples (Figure 1c), and the percentage of wines that verified the equation was satisfactory (Table 3), although the relationship between the experimental and model values was not significant (Table 3).

In this group of samples there was also reciprocal regression between HM and  $\Sigma$  ( $r = -0.5501$ ;  $p < 0.0001$ ).

**Table 2. Multiple Regression Equations between Wine Characteristics and Foam Properties of All Wines ( $n = 96$ )**

independent variable	HM coeff	$\Sigma$ coeff
constant	428.56	-1416.24
volatile acidity	-328.88	-18.39
density		1.45
total SO <sub>2</sub>	-1.89	-0.07
free SO <sub>2</sub>	2.71	0.13
absorbance at 280 nm		0.02
conductivity		-8.64
proteins	5.37	
citric acid	-216.35	-31.85
malic acid		2.41
glucose	-52.02	
succinic acid	103.46	
lactic acid		2.07
glycerol	-12.62	
ethyl acetate	1.14	
methanol	0.96	0.03
isobutyl alcohol	-2.91	
isoamyl alcohols	-0.64	

Thus, the  $\Sigma$  of these wines could be obtained from the predicted values of HM with the equation of this regression:  $1/\Sigma = 0.0806 - 1.1366E-4 \times \text{HM}$ . However, the prediction of this foam parameter did not improve, because the equation had the same RMSEP (4 s) as in the previous equation, and there was no significant relationship between the model  $\Sigma$  and the respective experimental  $\Sigma$  (Table 3).

**Predictive Equations Obtained with Cloudy Wines.** The predictive equations of cloudy wine foaming could greatly help wine-makers, as they frequently buy cloudy wines from other cellars to produce cava. The application of these empirical equations could easily give information about the foam capacity of these other wines. Wine-makers who have filtered base wines would

be able to find the foam properties of these base wines from the foam characteristics of their cloudy wines, thanks to the relationship between foaming of cloudy wines and foam capacity of the respective filtered base wines (López-Barajas et al., 1998).

Table 4 shows the equations obtained to predict the Bikerman coefficient ( $\Sigma$ ) and surface tension (ST) of cloudy wines. Again, the RMSEP values (Table 3) were satisfactory, in comparison with the levels of  $\Sigma$  and ST of the samples (Figure 1, parts b and c, respectively); there were significant regressions between the predicted and the experimental foam parameters, and the percentages of predicted wines were also satisfactory (Table 3).

Foamability (HM) of cloudy wines could be obtained from the predicted values of the Bikerman coefficient ( $\Sigma$ ), because in this group of samples there was a linear relationship between HM and  $\Sigma$  ( $r = 0.6529$ ;  $p < 0.0001$ ). The equation of this regression was  $\text{HM} = 13.5046 - 59.4155\Sigma$ .

**Predictive Equations Obtained with Wines from the Same Grape Variety.** Predictive equations were established to determine each foam parameter of Macabeo, Xarel.lo, and Parellada wines (Tables 3 and 4). These equations had the highest R-SQ (Tables 1 and 4). However, most of their RMSEP values were higher than the ones of the previous equations.

In conclusion, some empirical equations to predict the foam capacity of sparkling base wines, with the parameters of wine quality control, were established. Wine-makers could rapidly apply these equations and so have information about foaming of wines without any specific measurement of foam.

Among all of these predictive equations, the ones obtained with all wines [from different grape varieties, years of harvest, and wineries, and at different stages

**Table 3. Results of Multiple Regression Models of Foam Parameters [Foamability (HM), Bikerman Coefficient ( $\Sigma$ ), and Surface Tension (ST)] of the Wines Grouped According to Their Qualitative Characteristics (Winery and Type of Wine)**

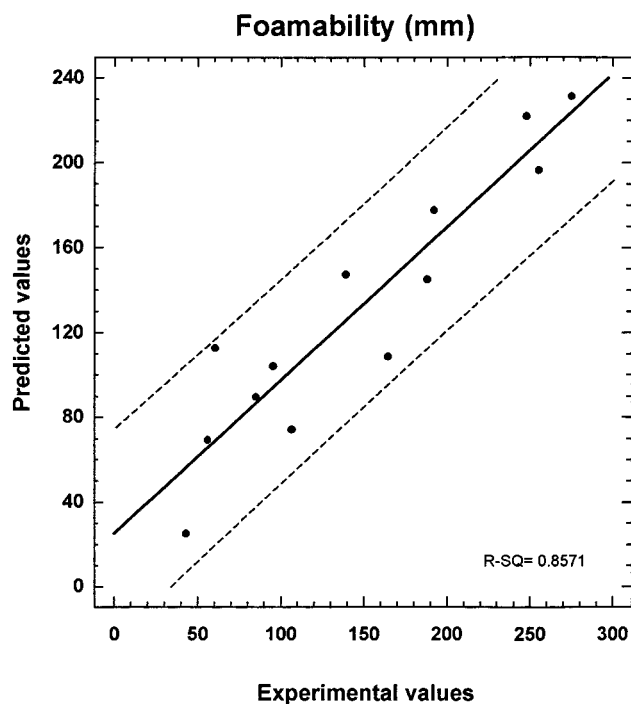
group of samples	predicted foam parameter	prediction R-SQ <sup>a</sup>	no. of parameters of the equation <sup>b</sup>	validation regr (mod-exp) <sup>c</sup> $r$ ; $p$	% of prediction <sup>d</sup>	RMSEP <sup>e</sup>
wines from the same winery ( $n = 66 \times 3^f$ )	HM	0.8486	9	$r = 0.9258$ ; $p < 0.0001$	38	35
data set: 53 wines	$\Sigma$	0.3025	reciprocal regr ( $\Sigma$ vs HM) <sup>g</sup>	$p > 0.05$	69	4
validation set: 13 wines	ST	0.6315	9	$p > 0.05$	70	1.7
prediction with cloudy wines ( $n = 48 \times 3^f$ )	HM	0.4263	linear regr (HM vs $\Sigma$ ) <sup>h</sup>	$r = 0.5546$ ; $p = 0.0015^i$	20	85
data set: 38 wines	$\Sigma$	0.6185	8	$r = 0.3807$ ; $p = 0.0379^i$	70	4
validation set: 10 wines	ST	0.6051	7	$r = 0.4114$ ; $p = 0.0239^i$	70	2.4
prediction with wines from the same grape variety						
Macabeo wines ( $n = 28 \times 3^f$ )	HM	0.9777	8	$r = 0.8993$ ; $p < 0.0001^j$	0	51
data set: 22 wines	$\Sigma$	0.8380	8	$r = -0.5583$ ; $p = 0.0160^k$	50	5
validation set: 6 wines	ST	0.7756	8		67	3.3
Xarel.lo wines ( $n = 28 \times 3^f$ )	HM	0.9793	17	$r = 0.6688$ ; $p = 0.0024$	33	53
data set: 22 wines	$\Sigma$	0.6601	4	$p > 0.05$	50	3
validation set: 6 wines	ST	0.8583	12	$p > 0.05$	50	3.1
Parellada wines ( $n = 28 \times 3^f$ )	HM	0.8803	9	$p > 0.05$	17	97
data set: 22 wines	$\Sigma$	0.8039	9	$p > 0.05$	50	5
validation set: 6 wines	ST	0.6934	7	$p > 0.05$	67	2.4

<sup>a</sup> R-square (R-SQ). <sup>b</sup> Number of parameters of the equation. <sup>c</sup> Regression coefficient ( $r$ ) and significance level ( $p$ ) of the relation between the model and the experimental values of the foam parameter. <sup>d</sup> Percentage of well-predicted samples. <sup>e</sup> Root mean standard error of prediction. <sup>f</sup> The three results obtained for every parameter in each wine were considered. <sup>g</sup> The prediction of  $\Sigma$  was established from the reciprocal regression (HM vs  $\Sigma$ ). <sup>h</sup> The prediction of HM was established from the lineal regression ( $\Sigma$  vs HM). <sup>i</sup> Multiplicative model regression. <sup>j</sup> Exponential model regression. <sup>k</sup> Reciprocal model regression.

**Table 4. Multiple Regression Equations between Wine Characteristics and Foam Properties of the Wines Grouped According to Their Qualitative Characteristics (Winery, Type of Wine, and Grape Variety)**

independent variable	wines from the same winery ( $n = 66 \times 3^a$ )		cloudy wines ( $n = 48 \times 3^a$ )	
	HM coeff	ST coeff	$\Sigma$ coeff	ST coeff
constant	23.57	50.12	0.39	74.61
ethanol content		-1.20	-1.80	-1.84
pH	102.60		9.52	
titratable acidity		4.23	1.58	
volatile acidity			-12.90	
free SO <sub>2</sub>		-0.27	0.06	0.04
absorbance at 280 nm	-0.20			
conductivity		-5.51		5.01
proteins	4.91	0.22	0.34	
total polysaccharides				0.01
acidic polysaccharides				-0.04
citric acid		11.41	-29.94	
galacturonic acid		-4.85		
malic acid				1.69
succinic acid	62.10			
lactic acid		2.89		1.87
glycerol	-28.47			
ethyl acetate	0.97	0.02		
methanol			0.11	
propanol	3.70			
isobutyl alcohol	-5.50			
isoamyl alcohols	-0.51			

<sup>a</sup> The three results obtained for every parameter in each wine were considered.



**Figure 3.** Simple regression between the predicted values and the experimental values of foamability (HM), in the one-fifth of wines from the same winery ( $n = 13$ ).

of the wine-making process (cloudy wines and filtered wines)] could be the most useful ones because these equations were able to predict different levels of foam properties (foamability and foam stability) in wines from any origin.

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