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Analytical Methods

Estimation of water activity from pH and °Brix values of some food products

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Abstract

In this study, a predictive model for the estimation of water activity ($a_w^{25\,°C}$) as a function of pH (1.00–8.00) and °Brix (0–82.00) values of simulated food solutions (SFS) was developed, through response surface methodology. Response fit analyses resulted in a highly significant (pH < 0.0001) square root polynomial model that can predict $a_w^{25\,°C}$ of SFS in terms of pH and °Brix values within the defined variable ranges. The linear, quadratic and interactive influences of pH and °Brix on $a_w^{25\,°C}$ were all significant (pH < 0.0001). Model validations in SFS and in a number of actual food systems showed that the model had acceptable predictive performance, as indicated by the calculated accuracy and bias indices.

Keywords: °Brix; pH; Predictive modelling; Response surface methodology (RSM); Soluble solids; Water activity

1. Introduction

Water activity (a_w) is a measure of the amount of water available for chemical reactions, as well as microbial growth in food (Belitz & Grosch, 1999; Jay, 2000; Rockland & Beuchat, 1987; Troller & Christian, 1978). Furthermore, the mode and severity of food processing for several commodities may be highly dependent on the a_w of the product (Zapsalis, 1985). Therefore, measurement of a_w is essential to the food industry, since it plays a vital role in addressing the needs for product stability, quality maintenance and sustaining the safety of food throughout its shelf-life. Sucrose is a common ingredient of many food products and used as sweetener or a humectant (Triebold & Aurand, 1963; Troller & Christian, 1978). Shelf-life stability of jams, marmalades, fruits in syrups, and other sweetened food products rely on the ability of sucrose to reduce the a_w to a level where microbial growth and unwanted chemical reaction rates are slowed down.

One major factor that influences a_w is the concentration and type of solute present in the food system (Fennema, 1996; Nielsen, 1994). Generally, by simply following Raoult's Law of mole fraction, increase in the amount of solute in a system shall ideally result in a predictable decrease in a_w (Fennema, 1996; Holtzclaw & Robinsons, 1988; Troller & Christian, 1978). Jay (2000), however, cited that many solutes, including the disaccharide sucrose, do not follow Raoult's Law. Interactions of several food properties may possibly explain such a phenomenon. For example, addition of acids in a system containing sucrose causes sugar inversion (Andrews, Godshall, & Moore 2002; Bennion, 1985; McWilliams, 1993). Invert sucrose has been reported to have a greater a_w-lowering effect on foods than sucrose alone (Fennema, 1996).

Despite being one of the more important food parameters that affect food quality and safety, micro- to medium-scale food processors are not able to afford a_w meters. Prices of the least expensive a_w meter models can be as much as US$2000 (Cole-Parmer Instrument Company. Water activity meter systems., 2007; Decagon

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Devices. Water activity for food science: assuring safety & governmental compliance., 2007; Novasina. Water activity: For applications in the food & cosmetic industry., 2007). Furthermore, operation of a_w meters may also be a concern, since stakeholders often lack manpower with sufficient technical knowledge. This study, therefore, tried addressing this gap, by developing a mathematical model capable of predicting the a_w at fixed temperature ($a_w^{25\,°C}$) of some foods, from easily measured, pertinent physicochemical food properties, namely pH and °Brix values. The study established a predictive model in simulated food solutions (SFS), which contained varying levels of water, sucrose and acid. The predictive performance of the established model was assessed through validations using a different set of SFS and various actual food systems.

2. Materials and methods

2.1. Simulated food solutions

The SFS were formulated based on the data supplied to and processed using the Design Expert Version 7.0.3 software package (Statease, Minneapolis, MN). A Central Composite Rotatable Design (CCRD) was applied, to determine the appropriate combinations of various levels of pH and °Brix. Table 1 presents the coded and uncoded SFS formulations that resulted from the CCRD. The assigned °Brix values per SFS were achieved by dissolving food grade D-sucrose (Ajax Finechem, Australia) in de-ionised distilled water. The desired pH value per SFS was adjusted using 5 N HCl (Himedia, Mumbai, India) or 8 N NaOH (Himedia). Freshly prepared solutions were immediately subjected to a_w analyses.

Table 1
Rotatable central composite design used in the formulation of simulated food solutions

Experimental runs[a]	Blocks	Coded variable combinations		Uncoded variable combinations	
		pH	°Brix	pH	°Brix
6	1	0	0	4.50	41.00
5	1	0	0	4.50	41.00
1	1	−1	−1	2.00	12.00
4	1	+1	+1	7.00	70.00
2	1	+1	−1	7.00	12.00
3	1	−1	+1	2.00	70.00
7	1	0	0	4.50	41.00
11	2	0	+α	4.50	82.00
13	2	0	0	4.50	41.00
14	2	0	0	4.50	41.00
8	2	−α	0	1.00	41.00
12	2	0	0	4.50	41.00
9	2	+α	0	8.00	41.00
10	2	0	−α	4.50	0.00

[a] Experimental runs are presented according to the established randomized order of the design of experiment.

2.2. Measurement of a_w

The Novasina™ ms1 set aw (Novasina, Pfaffikon, Switzerland) was used to measure the water activity of the samples at 25 °C ($a_w^{25\,°C}$). Prior to using the device, the instrument was calibrated using saturated salt solutions of known relative humidity (RH) standards namely, 11.3%, 32.8%, 52.9%, 75.3%, and 90.1% RH. After the calibration, 5.0 ml of the sample was placed inside the measuring chamber and the head sensor was fitted to seal the chamber. The $a_w^{25\,°C}$ values were obtained with ±0.01 accuracy. Measurements were done in triplicate.

2.3. Predictive model development and analysis

The general form of the quadratic polynomial model equation used in the study is presented in Eq. (1) (Adinarayana & Ellaiah, 2002; Han, Floros, Linton, Nielsen, & Nelson, 2002). This equation contains linear terms x_1 and x_2, which correspond to the physicochemical properties pH and °Brix, respectively. Square (x_1^2 and x_2^2) and interaction ($x_1 \times x_2$,) terms are also included in the equation. The y value corresponds to the response variable, $a_w^{25\,°C}$, while the β terms are regression coefficients.

$$Y = \beta_0 + \beta_1(x_1) + \beta_2(x_2) + \beta_{1\times 2}(x_1 \times x_2) + \beta_{1\times 1}(x_1^2) + \beta_{2\times 2}(x_2^2) \tag{1}$$

The $a_w^{25\,°C}$ measured from the test SFS were subjected to response surface model fitting (Adinarayana & Ellaiah, 2002). Data analyses were conducted using the Design Expert Version 7.0.3 (Statease, Minneapolis, MN) software package. The response surface plotted to demonstrate the influences of the predictive variables on the response was constructed using STATISTICA software package, 1999 version (Statsoft, Inc., Tulsa, OK).

2.4. Model validation

The predictive performance of the derived model was validated in a separate set of SFS with pH and °Brix values different from those identified by the CCRD. A number of appropriate actual food systems were also used in validating the performance of the model. Freshly prepared validating SFS with randomly assigned physicochemical properties (Table 5) were subjected to $a_w^{25\,°C}$ analyses following the previously detailed methods. For actual food systems, 5.0 ml or 5.0 g of the food sample was similarly subjected to $a_w^{25\,°C}$ measurement. The pH and °Brix values of the validating SFS and food systems were measured and factored into the developed model to calculate the predicted $a_w^{25\,°C}$ (${}^{p}a_w^{25\,°C}$). The $a_w^{25\,°C}$ values measured by the a_w meter (${}^{a}a_w^{25\,°C}$) were then compared with the ${}^{p}a_w^{25\,°C}$, to assess the predictive performance of the model.

The mathematical predictive model assessments were done by calculating the model performance indices, accuracy factor (A_f) and bias factor (B_f), defined by Ross

(1996) and Baranyi, Pin, and Ross (1999), and similarly used by McElroy, Jaykus, and Foegeding (2000), Tejedor, Rodrigo, and Martinez (2001), Wei, Fang, and Chen (2001), Cayré, Vignolo, and Garro (2003), Jagannath and Tsuchido (2003), Carrasco et al. (2006), and Mataragas, Drosinos, Vaidanis, and Metaxopolous (2006). The B_f estimated the mean difference between the ${}^{\mathrm{p}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ and the ${}^{\mathrm{a}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ and was calculated using:

$$B_f = 10^{\left\{\frac{\sum\left[\log_{10}\frac{{}^{\mathrm{p}}a_{\mathrm{w}}}{{}^{\mathrm{a}}a_{\mathrm{w}}}\right]}{n}\right\}} \tag{2}$$

where n corresponds to the number of replications employed in the model validation process. The B_f assessed whether the model over- or under estimated the $a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ of the validating SFS or food systems. When $B_f < 1.00$, the model underestimated the $a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ of the validating system while $B_f > 1.00$ values are indicative of model overestimations. A B_f value of 1.00 signifies that the ${}^{\mathrm{p}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ and the ${}^{\mathrm{a}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ are in perfect agreement. Since the B_{f} value does not provide an indication of model predictive accuracy, the A_f was also calculated:

$$A_f = 10^{\left\{\frac{\sum\left|\log_{10}\frac{{}^{\mathrm{p}}a_{\mathrm{w}}}{{}^{\mathrm{a}}a_{\mathrm{w}}}\right|}{n}\right\}} \tag{3}$$

Take note that the only difference between Eqs. (2) and (3) is that A_f value measures the mean absolute difference between the ${}^{\mathrm{p}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ and the ${}^{\mathrm{a}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$. The A_f takes values > 1.00, where greater A_f values are indicative of less model predictive accuracy. An $A_f = 1.00$ is also an indication of perfect agreement between the predicted and actual values.

Thus for cases where ${}^{\mathrm{p}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}} > {}^{\mathrm{a}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$, the calculated A_f and B_f values will be equal, since both $\log_{10}$ and $|\log_{10}|$ of $({}^{\mathrm{p}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}/{}^{\mathrm{a}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}})$ result in the same positive number. However, when ${}^{\mathrm{p}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}} < {}^{\mathrm{a}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$, the $\log_{10}$ and $|\log_{10}|$ of the quotient of the predicted and actual ${}^{\mathrm{a}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ values shall result in numbers with the same value but opposite signs; hence $A_f \neq B_f$.

Graphical comparisons of the predicted and actual calculated $a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ were also done by plotting ${}^{\mathrm{p}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ against ${}^{\mathrm{a}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$. The line of equivalence (LOE) was traced, to indicate the region of the plot where ${}^{\mathrm{p}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}} = {}^{\mathrm{a}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$. The LOE is the line with an equation y = x and diagonally bisects the plot into two equal regions. A point falling on the LOE has $A_f = B_f = 1.00$, hence perfect agreement between ${}^{\mathrm{p}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ and ${}^{\mathrm{a}}a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$. Points falling above ($A_f = B_f > 1.00$) and below ($A_f > 1.00$, $B_f < 1.00$) have been overestimated and underestimated by the model, respectively. The farther the point from the LOE, the greater the A_f and B_f values will be. Thus the positions of the plotted points, with respect to the LOE, may also be used as bases in the evaluation of the performance of the predictive model.

3. Results and discussion

3.1. Predictive model fitting and analysis

Table 2 presents the $a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ measured from the different SFS with varying pH and °Brix combinations. With these results, it can clearly be seen that both predictive variables influenced the measured response. SFS with higher °Brix values had lower a_{w} than those with lower °Brix, at a fixed pH level. The effect of differing pH on the a_{w} of SFS with equal °Brix was also demonstrated. The significance of these influences and the possible existence of non-linear and interactive predictive variable influences were further explored and are discussed in the following sections.

Table 2
Water activity[a] of simulated food solutions of varying pH and °Brix values

Physicochemical variable combinations		$a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$
pH	°Brix	
4.50	41.00	0.966 ± 0.006
4.50	41.00	0.975 ± 0.004
2.00	12.00	1.000 ± 0.003
7.00	70.00	0.864 ± 0.002
7.00	12.00	0.988 ± 0.011
2.00	70.00	0.787 ± 0.010
4.50	41.00	0.977 ± 0.006
4.50	82.00	0.732 ± 0.013
4.50	41.00	0.972 ± 0.004
4.50	41.00	0.973 ± 0.007
1.00	41.00	0.922 ± 0.013
4.50	41.00	0.973 ± 0.005
8.00	41.00	0.968 ± 0.002
4.50	0.00	0.995 ± 0.002

[a] a_{w} were measured at 25 °C using a Novasina™ ms1-aw (Novasina, Switzerland) water activity meter. Values are presented as averages of three trials ± standard deviation.

The influences of pH and °Brix on SFS $a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ were quantitatively and qualitatively characterised by fitting the obtained results (Table 2) into a second-order polynomial model (Eq. (1)). This model was used to account for possible non-linear relationships between the predictive and response variables (Mendenhall & Sincich, 1996). Hu (1999) explained that lower degree polynomial models, such as those with interaction and quadratic terms, are appropriate to adequately describe food processes. Results of the Box-Cox power transform analysis (Design Expert 7.0.3, Statease) of model fit on Eq. (1) (current λ = 1.00, best λ = 2.48) however suggested that the results obtained from the study had better fit on Eq. (4) (current λ = 1.00, best λ = 1.22).

$$Y^2 = \beta_0 + \beta_1(x_1) + \beta_2(x_2) + \beta_{1\times 2}(x_1 \times x_2) + \beta_{1\times 1}(x_1^2) + \beta_{2\times 2}(x_2^2) \tag{4}$$

The results of the second order model fitting on Eq. (4) are presented in Table 3. The Fisher F-test results with very low p-values demonstrated the very high significance of the model and conveys that the predictive variables, pH and °Brix, can be used to reliably predict the response variable, $a_{\mathrm{w}}^{25\,^{\circ}\mathrm{C}}$ (Adinarayana & Ellaiah, 2002; University of California at Los Angeles, 2006). In Table 3, it is also shown that the predictive variables have non-linear and interactive influences on the response. Thus, utilisation of model Eq. (4) was deemed appropriate. Further, the high lack-of-fit F-value implied that the obtained results fitted well to the model equation.

Table 3
Analysis of variance for the response surface model

Source	Sum of squares	Df	Mean square	F-value	p-value
Model	2.70×10^{-1}	5	5.40×10^{-2}	772.5	<0.0001 s
pH	6.39×10^{-3}	1	6.39×10^{-3}	91.2	<0.0001 s
°Brix	2.00×10^{-1}	1	2.00×10^{-1}	2803.5	<0.0001 s
pH×°Brix	5.70×10^{-3}	1	5.70×10^{-3}	81.4	<0.0001 s
pH^2	4.49×10^{-3}	1	4.49×10^{-3}	64.2	<0.0001 s
$°Brix^2$	6.00×10^{-2}	1	6.00×10^{-2}	852.8	<0.0001 s
Residual	4.90×10^{-4}	7	7.00×10^{-5}		
Lack of fit	2.13×10^{-4}	3	7.09×10^{-5}	1.0	0.4712 ns
Pure error	2.77×10^{-4}	4	6.93×10^{-5}		

s: significant; ns: not significant at 95% level of significance.

Table 4
Statistics used in model goodness-of-fit evaluation

Statistics	
Coefficient of variation (%CV)	0.950
Correlation coefficient, r	0.999
Determination coefficient, r^2	0.998
Adjusted r^2	0.997
Predicted r^2	0.991
Adequate precision	77.224

The statistics (Table 4) used to evaluate the goodness of fit of the model further support the result obtained by the F-test. The calculated coefficient of variation (% CV) was low and served as an indication of the precision and reliability of the experiments conducted in the study (Adinarayana & Ellaiah, 2002). At the same time, the high value of the correlation coefficient (r) also indicated the strong association between the response and the independent variables (Box, Hunter, & Hunter, 1978). The values of the determination coefficient (r^2) and adjusted r^2 indicate that the model can predict and explain the total variations in the measured response by 99.8 and 99.7%, respectively (Adinarayana & Ellaiah, 2002; University of California at Los Angeles, 2006). The predicted r^2 was in reasonable agreement with the adjusted r^2 and the calculated statistics for adequate precision indicated a desirable signal-to-noise ratio. Hence the predictive model was deemed suitable to be used to navigate the experimental design space.

3.2. Influences of pH and °Brix on $a_w^{25\,°C}$

Eq. (5) presents the final predictive equation for $a_w^{25\,°C}$, in terms of pH and °Brix values. This equation includes the individual linear and quadratic and interactive influences of the predictive variables on the response. When charted on a 3-dimensional plot, the response surface that shows the change in $a_w^{25\,°C}$, as pH and °Brix values vary, is presented in Fig. 1. In this figure, the quick descent of the response surface plot with increasing °Brix value, compared to the gradual ascent of the plot with increasing pH value, is indicative of the greater influence of the latter variable on $a_w^{25\,°C}$:

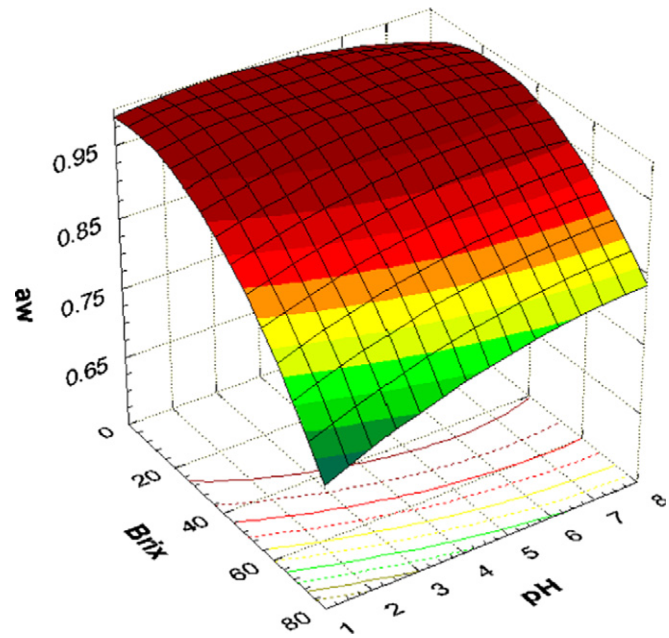

Fig. 1. Response surface plot showing the influences of pH and °Brix on $a_w^{25\,°C}$.

$$a_w^{25°\,C} = [0.95 + 0.03(\text{pH}) + 1.02 \times 10^{-3}(°\text{Brix}) + 5.21 \times 10^{-4}(\text{pH} \times° \text{Brix}) - 3.95 \times 10^{-3}(\text{pH}^2) - 1.07 \times 10^{-4}(°\text{Brix}^2)]^{1/2} \tag{5}$$

In Fig. 1, it is demonstrated that, at any fixed pH value, $a_w^{25\,°C}$ decreased with increasing °Brix value. Most a_w meters measure the vapour pressure of water present in the sample being analysed (Troller & Christian, 1978) and an increased amount of dissolved solutes in a food system has been recognised to cause reduction in a_w. Baianu (1992) and Fennema (1996) explained that in a particular aqueous system, dissolution of solutes like sucrose results in the reduction of water vapour pressure, due to the binding of water molecules to the solute molecules. Hence, this reduction in the total vapour pressure of the system results in the reduction in the a_w of the system.

Furthermore, at any value from 1 to 80 °Brix, reduction in pH resulted in a reduction in $a_w^{25\,°C}$. Such a phenomenon may be explained by the acid-mediated cleavage of

Table 5
Model validation in simulated food solutions

Validating SFS	SFS properties[A]		$a_w^{25\,°C}$			Performance indices	
	pH	°Brix	${}^{p}a_w$	${}^{a}a_w$	Δa_w[B]	A_f	B_f
1	1.00	10.00	0.99	0.96	0.03	1.03	1.03
2	2.00	50.00	0.91	0.95	−0.04	1.05	0.96
3	3.00	70.00	0.81	0.85	−0.04	1.05	0.95
4	4.00	20.00	1.01	0.99	0.02	1.01	1.01
5	7.00	30.00	0.99	0.97	0.02	1.02	1.02

[A] Values are reported as mean values of three trials.
[B] Calculated by subtracting the actual (${}^{a}a_w^{25\,°C}$) from predicted (${}^{p}a_w^{25\,°C}$) in each SFS.

glycosidic bonds, which link the monomeric components of sucrose (Andrews et al., 2002; Aurand & Woods, 1973; Gibson, 1973). Lowering the pH of the SFS promotes the conversion of sucrose to glucose and fructose, inducing further decrease in a_w. Theoretically, complete hydrolysis of 1 mole of sucrose shall result in 2 moles of monosaccharides, increasing the a_w-lowering effect by about two times (Stallenberger & Birch, 1995). At 0 °Brix, slight reduction

Table 6
Model validation on real food systems

Food systems	Food properties[A]		$a_w^{25\,°C}$			Performance indices	
	pH	°Brix	${}^{p}a_w$	${}^{a}a_w$	Δa_w[B]	A_f	B_f
Fruit juices and juice drinks							
Orange juice (Brand 1)	4.38	11.60	1.01	1.00	0.01	1.01	1.01
Orange juice (Brand 2)	4.04	13.22	1.01	1.00	0.01	1.01	1.01
Sweetened orange juice	3.30	14.13	1.01	0.97	0.04	1.04	1.04
Ruby grapefruit juice	3.56	11.78	1.01	0.99	0.02	1.01	1.01
Philippine orange juice drink	4.08	11.80	1.01	0.99	0.02	1.01	1.01
Philippine lemon juice drink	3.98	12.60	1.01	0.98	0.03	1.03	1.03
Apple juice	3.62	12.60	1.01	1.00	0.01	1.01	1.01
Apple juice drink	3.79	11.20	1.01	1.00	0.01	1.01	1.01
Pineapple juice (Brand 1)	4.71	12.60	1.01	0.98	0.03	1.03	1.03
Pineapple juice (Brand 2)	4.62	13.40	1.01	0.99	0.02	1.01	1.01
Grape juice	3.58	15.91	1.01	0.97	0.04	1.03	1.03
Mango juice drink (Brand 1)	4.26	12.40	1.01	0.99	0.02	1.02	1.02
Mango juice drink (Brand 2)	3.89	12.80	1.01	0.99	0.02	1.02	1.02
Soursop juice drink	4.55	13.78	1.01	0.99	0.02	1.02	1.02
Guava juice drink	4.52	12.40	1.01	0.97	0.04	1.04	1.04
Peach juice drink	3.67	12.40	1.01	0.97	0.04	1.04	1.04
Fruit nectars and concentrates							
Mango nectar	4.31	12.38	1.01	1.00	0.01	1.01	1.01
Guava nectar	3.58	11.60	1.01	1.00	0.01	1.01	1.01
Soursop nectar	4.73	12.00	1.01	0.98	0.03	1.03	1.03
Philippine lemon concentrate	2.50	63.06	0.84	0.83	0.01	1.02	1.02
Philippine orange concentrate	2.84	51.34	0.92	0.91	0.01	1.01	1.01
Jams, jellies and similar products							
Pineapple jam	3.02	54.26	0.91	0.84	0.07	1.08	1.08
Mango jam	2.97	64.40	0.85	0.77	0.08	1.10	1.10
Guava jelly	3.37	68.66	0.83	0.77	0.06	1.07	1.07
Orange marmalade	3.07	63.06	0.86	0.79	0.07	1.08	1.08
Young coconut strings in syrup	4.07	50.80	0.94	0.93	0.01	1.00	1.00
Coconut gel (nata de coco) in syrup	5.84	34.27	0.99	0.98	0.01	1.01	1.01
Palm nut in syrup	6.13	26.97	1.00	0.98	0.02	1.02	1.02
Sweetened purple yam	5.49	68.80	0.86	0.94	−0.08	1.10	0.91
Dried fruits							
Raisins	3.70	66.00	0.85	0.71	0.14	1.20	1.20
Prunes	4.07	67.80	0.84	0.82	0.02	1.04	1.04
Mangoes	3.74	75.47	0.78	0.71	0.07	1.10	1.10
Apricots	3.79	64.41	0.86	0.83	0.03	1.03	1.03
Papaya	3.78	79.50	0.75	0.68	0.07	1.10	1.10
Cantaloupe	3.83	65.40	0.86	0.70	0.16	1.22	1.22
Pineapple	4.07	62.0	0.88	0.71	0.17	1.23	1.23
Milk and dairy products							
Fresh milk (UHT-processed)	6.09	12.53	1.00	1.00	0.00	1.00	1.00
Evaporated milk	6.31	25.67	1.00	1.00	0.00	1.00	1.00
Reconstituted filled milk	6.29	29.60	1.00	1.00	0.00	1.00	1.00
Condensed milk	6.59	74.40	0.83	0.89	−0.06	1.08	0.93
Milk chocolate drink	6.51	18.67	1.00	1.00	0.00	1.00	1.00
Other food products							
Apple and cereal-based baby food	3.91	20.97	1.00	0.98	0.02	1.02	1.02
Pear and cereal-based baby food	3.96	16.10	1.01	0.99	0.02	1.02	1.02
Mayonnaise	3.46	0.87	1.00	0.97	0.03	1.03	1.03

[A] Values are reported as mean values of three trials.
[B] Calculated by subtracting the actual (${}^{a}a_w$) from predicted (${}^{p}a_w$) in each real food system.

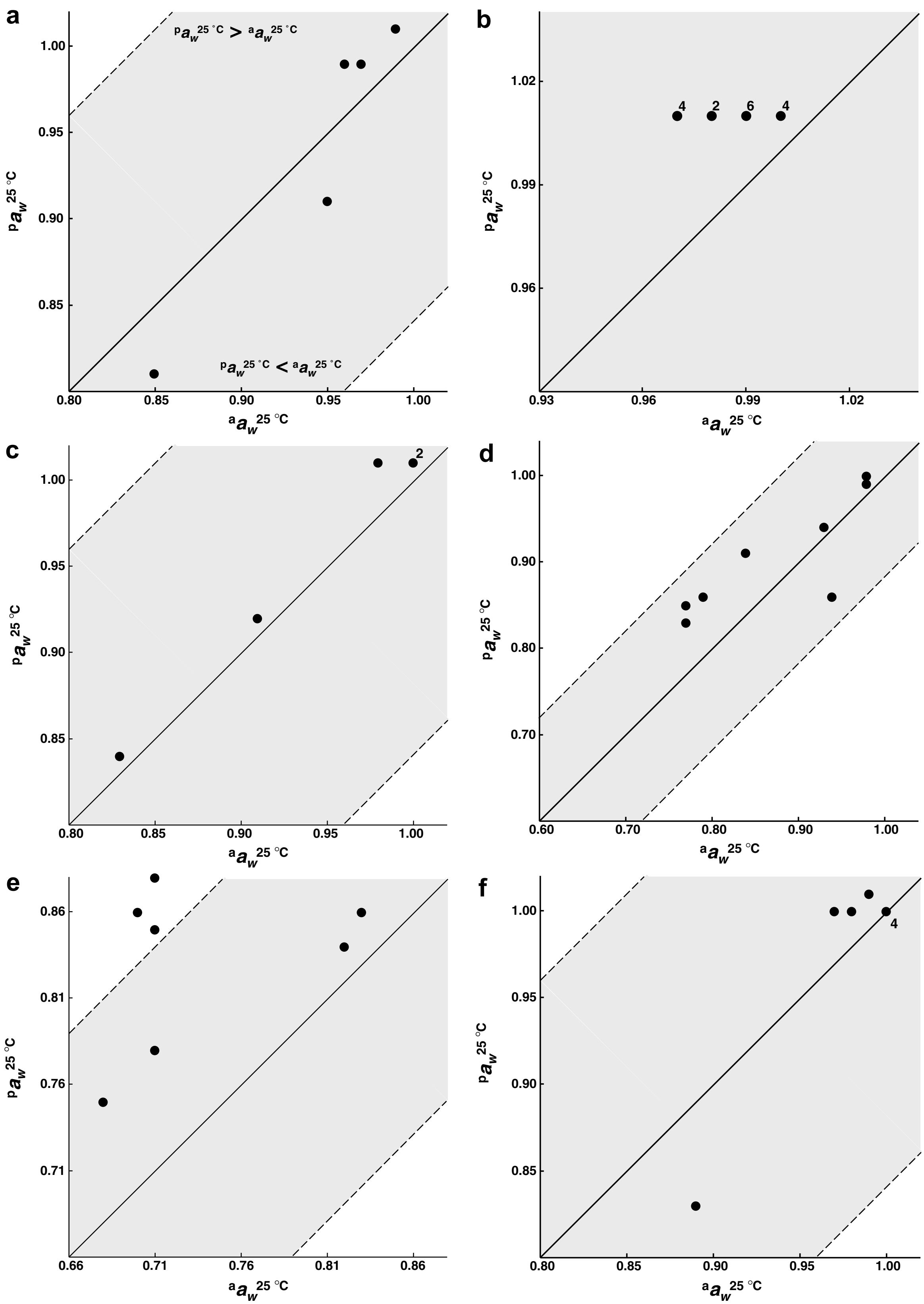

Fig. 2. Graphical comparisons between the model-generated $^{p}a_w^{25\,°C}$ and actual measured $^{a}a_w^{25\,°C}$ in: (a) the validating simulated food systems, (b) fruit juices and juice drinks, (c) fruit nectars and concentrates, (d) jams, jellies and similar products, (e); dried fruits, and (f) milk, dairy products and other food products. The numbers placed near the points indicate the number of points that coincided in the same coordinates. The line bisecting each plot, the line of equivalence (LOE) denotes the region where $^{p}a_w^{25\,°C} = {}^{a}a_w^{25\,°C}$, while the shaded areas bound by the dotted lines indicate the $\pm$ 20% prediction error regions where $A_f > 1.20$.

of $a_w^{25\,^\circ C}$ with increasing pH might have been due to the increase in the ions contributed by the concentrated NaOH used to adjust the SFS pH.

3.3. Model validation

A predictive model may only be safely used in decision making when validated (Jagannath & Tsuchido, 2003). Validation is an essential step that reveals the applicable range of a model and the limits of its performance. Therefore this study also dealt with the validation of the developed model, using a set of data obtained from additional test runs, exclusive from those performed in the elaboration of the model, as recommended by Ross (1996) and Carrasco et al. (2006). In this new study, the reliability of the developed model was also assessed through validations in real food systems, as similarly done by McElroy et al. (2000), and Jagannath and Tsuchido (2003).

Tables 5 and 6 present the calculated values of the performance indices for the validation of the additional SFS and real food systems, respectively. In the validating set of SFS, the calculated A_f values varied from 1.01 to 1.05 (range: 0.04). Moreover, the A_f values calculated from model validations using actual food systems ranged from 1.00 to 1.23 (range: 0.23). Ross, Dalgaard, and Tienungoon (2000) reported that predictive models should ideally have $A_f = 1.00$, which indicates a perfect model fit where the predicted and actual response values are equal. However, Ross et al. (2000) and Carrasco et al. (2006) explained that, typically, the A_f of a model increases by 0.10–0.15 units for every predictive variable in the model. Therefore, a model that forecasts a response from two predictive variables may be expected to have A_f values that range from 1.20 to 1.30 (Ross et al., 2000) or an equivalent% error range of 20–30%. Therefore based on the results obtained from the validating SFS and actual food systems, the predictive performance of the established model may be considered acceptable.

The calculated B_f values ranged from 0.95 to 1.03 (range: 0.08) and 0.91 to 1.23 (range: 0.32) for SFS and actual food systems, respectively. These values indicate that the predictive model under- or over-estimated the actual a_w of the validating SFS and food systems. Jagannath and Tsuchido (2003) reported that higher B_f values may be expected, if a predictive model is validated in conditions different from those used in the model establishment. Thus, in their study, B_f values of 1.41 and 1.60 were considered acceptable after validating a phosphate buffer-based model in actual milk systems. As with the A_f values, slightly higher Bf values were calculated from validations in real food systems, compared to those calculated from the validating SFS. In all validating systems but two samples (sweetened purple yam and condensed milk), where the predictive model overestimated the $a_w^{25\,^\circ C}$, the A_f and B_f values were calculated to be equal.

The discrepancies between the ${}^{p}a_w^{25\,^\circ C}$ and ${}^{a}a_w^{25\,^\circ C}$ calculated from validations in SFS and different actual food systems are also illustrated in Fig. 2a–f. In the figure, it can be seen that only three (Fig. 2e) model predictions had% error values greater than 20% ($A_f > 1.20$). These points correspond to the $a_w^{25\,^\circ C}$ estimated for raisins, dried cantaloupe and dried pineapples. Nevertheless these points were still within a 30% error ($A_f < 1.30$), and hence can still be considered to have acceptable accuracy (Ross et al., 2000). These results agree with the calculated model performance indices. Parallel to the calculated performance indices, graphical validations showed that the model had better predictive performance in the SFS than in actual food systems (not emphasised in the figure). Such results may be expected (Jagannath & Tsuchido, 2003), since the model was established using SFS.

The greater differences between ${}^{p}a_w^{25\,^\circ C}$ and ${}^{a}a_w^{25\,^\circ C}$ in actual food systems may be due to the influences of other food components on the a_w that were not present in the SFSs used in establishing the model. Food components such as proteins, complex and simple carbohydrates, salts and other dissolved components might have caused such observations. Despite these variations, results of mathematical validations showed that the established predictive model reliably predicted the a_w of the validating systems. Hence, the predictive model may safely be used in calculating the a_w of appropriate food systems.

4. Summary and recommendations

This study dealt with the development of a predictive response surface model for the estimation of $a_w^{25\,^\circ C}$ from pH and °Brix values of appropriate food systems. The highly significant predictive model was developed from simulated food systems (SFS) but was validated using a separate set of SFS and actual food systems. Results of the validation showed that the developed model had acceptable predictive performance, as assessed by mathematical and graphical model performance indices. The study recommends further validation in other appropriate food products, so as to further explore the predictive capacity and limitations of the model. Other predictive variables such as temperature and types of solutes may also be considered in building up a more accurate and practical predictive model.

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References

Adinarayana, K., & Ellaiah, O. (2002). Response surface optimization of the critical medium components for the production of alkaline protease by newly isolated *Bacillus* sp.. *Journal of Pharmacy and Pharmaceutical Sciences, 5*(3), 272–278.

Andrews, L. S., Godshall, M. A., & Moore, S. (2002). Sucrose degradation under model processing conditions. *Journal of Food Science, 67*(5), 1621–1624.

Aurand, L. W., & Woods, A. E. (1973). *Food Chemistry*. Westport, CT: Avi Publishing Company, Inc.

Baianu, I. C. (1992). *Physical chemistry of food processes. Fundamental aspects* (Vol. 1). Leinhold: Van Nostrand.

Baranyi, J., Pin, C., & Ross, T. (1999). Validating and comparing predictive models. *International Journal of Food Microbiology, 49*, 159–166.

Belitz, H. D., & Grosch, W. (1999). *Food chemistry*. Berlin: Springer Verlag.

Bennion, M. (1985). *Introductory foods* (8th ed.). New York: Macmillan.

Box, G. E. P., Hunter, W. G., & Hunter, J. S. (1978). *Statistics for experimenters: An introduction to design, data analysis, and model building*. New York: John Wiley and Sons.

Carrasco, E., Garcia-Gimeno, R., Seselovsky, R., Valero, A., Perez, F., Zurera, G., et al. (2006). Predictive model of *Listeria monocytogenes'* growth rate under different temperatures and acids. *Food Science and Technology International, 12*(1), 47–56.

Cayré, M. E., Vignolo, G., & Garro, O. (2003). Modeling lactic acid bacteria growth in vacuum-packaged cooked meat emulsions stored at three temperatures. *Food Microbiology, 20*, 561–566.

Cole-Parmer Instrument Company. Water activity meter systems. (2007). <http://www.coleparmer.com/> Accessed 08.06.07.

Decagon Devices. Water activity for food science: assuring safety, quality and governmental compliance. (2007). <http://www.decagon.com/> Accessed 08.06.07.

Fennema, O. (1996). *Food chemistry* (2nd ed.). NY & Basel: Marcel Dekker Inc.

Gibson, B. (1973). The effect of high sugar concentrations on the heat resistance of vegetative microorganisms. *Journal of Applied Bacteriology, 36*, 365–376.

Han, Y., Floros, J. D., Linton, R. H., Nielsen, S. S., & Nelson, P. E. (2002). Response surface modeling for the inactivation of *Escherichia coli* O157:H7 on green peppers (*Capsicum annum*) by ozone gas treatment. *Journal of Food Science, 67*(3), 1188–1193.

Holtzclaw, H., & Robinsons, W. (1988). *General Chemistry*. D.C. Heath & Company.

Hu, R. (1999). *Food product design: A computer-aided statistical approach*. USA: Technomic Publishing Co. Inc.

Jagannath, A., & Tsuchido, T. (2003). Validation of a polynomial regression model: the thermal inactivation of *Bacillus subtilis* spores in milk. *Letters Applied Microbiology, 37*, 399–404.

Jay, J. M. (2000). *Modern food microbiology* (6th ed.). Singapore: APAC Publishers.

Mataragas, M., Drosinos, E. H., Vaidanis, A., & Metaxopolous, I. (2006). Development of a predictive model for the spoilage of cooked cured meat products and its validation under constant and dynamic temperature storage conditions. *Journal of Food Science, 71*, 157–167.

McElroy, D. M., Jaykus, L., & Foegeding, P. M. (2000). Validation and analysis of modeled predictions of growth of *Bacillus cereus* spores in boiled rice. *Journal of Food Protection, 63*(2), 268–272.

McWilliams, M. (1993). *Food fundamentals*. New York: MacMillan Publishing Company.

Mendenhall, W., & Sincich, T. (1996). *A second course in statistics: Regression analysis* (5th ed.). New Jersey: Prentice Hall International, Inc.

Nielsen, S. (1994). *Introduction to the chemical analysis of foods*. Boston: Jones and Bartlett Publications.

Novasina. Water activity: For applications in the food, pharmaceutical and cosmetic industry. (2007). <http://www.novasina.ch/> Accessed 08.06.07.

Rockland, L., & Beuchat, L. (1987). *Water activity: Theory and applications to food*. New York: Marcel Dekker.

Ross, T. (1996). Indices for performance evaluation of predictive models in food microbiology. *Journal of Applied Bacteriology, 81*, 501–508.

Ross, T., Dalgaard, P., & Tienungoon, S. (2000). Predictive modeling of the growth and survival of *Listeria* in fishery products. *International Journal of Food Microbiology, 62*, 231–245.

Stallenberger, R. S., & Birch, G. G. (1995). *Sugar chemistry*. Westport, CT: Avi Publishing Company, Inc.

Tejedor, W., Rodrigo, M., & Martinez, A. (2001). Modeling the combined effect of pH and temperature on the heat resistance of *Bacillus stearothermophilus* spores heated in a multicomponent food extract. *Journal of Food Protection, 64*(10), 1631–1635.

Triebold, H., & Aurand, L. (1963). *Food composition and analysis*. Princeton, NJ: Van Nostrand.

Troller, J., & Christian, H. (1978). *Water activity and food*. New York: Academic Press.

University of California at Los Angeles, Academic Technology Services. Annotated SAS output: Regression analysis. (2006). <http://www.ats.ucla.edu/STAT/SAS/output/reg.htm/> Accessed 07.05.06.

Wei, Q. K., Fang, T. J., & Chen, W. C. (2001). Development and validation of growth model for *Yersinia enterocolitica* in cooked chicken meats packaged under various atmosphere packaging and stored at different temperatures. *Journal of Food Protection, 64*(7), 987–993.

Zapsalis, C. (1985). *Food chemistry and nutritional biochemistry*. New York: Wiley.