

4.1. WATER ACTIVITY

The desorption isotherms of meat with a different NaCl content at different temperatures are shown in Figures 4.1.1, 4.1.2, and 4.1.3. The experimental points and the isotherms predicted by the model type II (GAB and Mújica models with salt dependent coefficients and Clausius-Clayperon equation used to consider the temperature effect) are shown. The means of the NaCl contents of the samples were 0, 0.08, 0.2 and 0.31 kg/kg d.m. The experimental data are reported in appendix B.

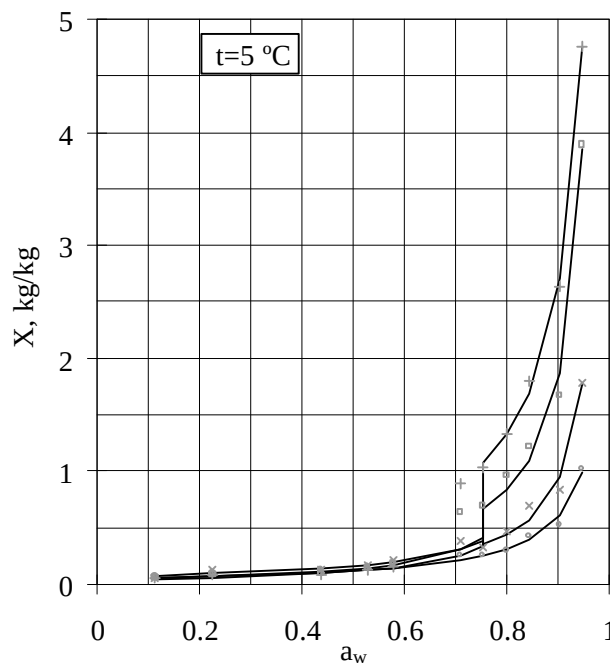


Figure 4.1.1 Calculated (—) and experimental (+, !, x, O) desorption isotherms at different NaCl content and at 5 °C (model type 2). X: water content (kg H₂O/kg d.m.). (O): meat 0 kg NaCl/kg d.m. (x) meat 0.08 kg NaCl/kg d.m. (!) meat 0.20 kg NaCl/kg d.m. (+) meat 0.31 kg NaCl/kg d.m.

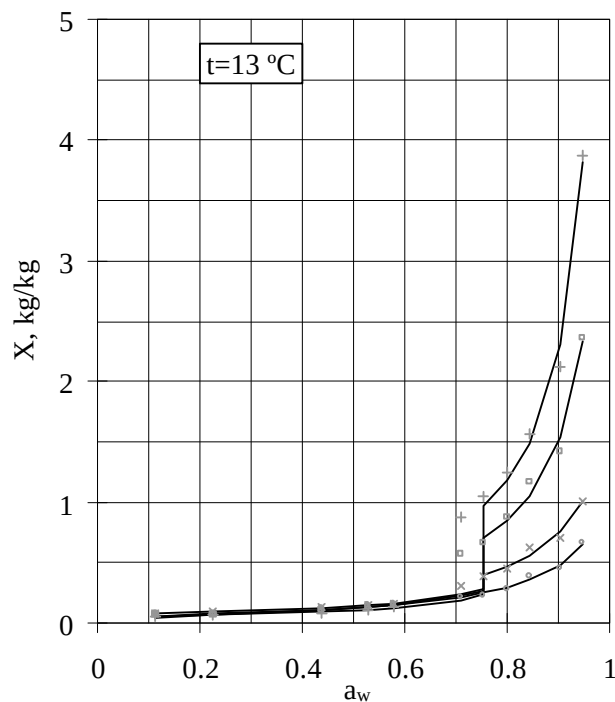


Figure 4.1.2 Calculated (—) and experimental (+, !, x, O) desorption isotherms at different NaCl content and at 13 °C (model type 2). X: water content (kg H₂O/kg d.m.). (O): meat 0 kg NaCl/kg d.m. (x) meat 0.08 kg NaCl/kg d.m. (!) meat 0.20 kg NaCl/kg d.m. (+) meat 0.31 kg NaCl/kg d.m.

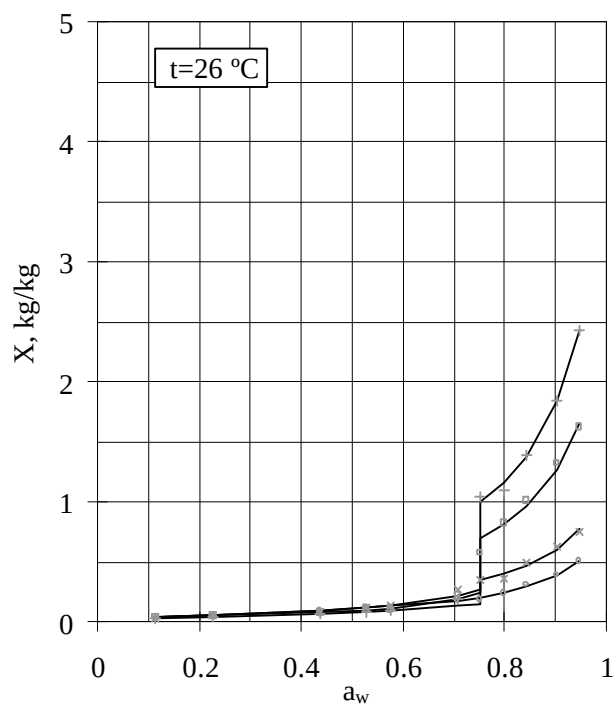


Figure 4.1.3 Calculated (—) and experimental (+, !, x, O) desorption isotherms at different NaCl content and at 26 °C (model type 2). X: water content (kg H₂O/kg d.m.). (O): meat 0 kg NaCl/kg d.m. (x) meat 0.08 kg NaCl/kg d.m. (!) meat 0.20 kg NaCl/kg d.m. (+) meat 0.31 kg NaCl/kg d.m.

A drop of the isotherm for salted meat around $a_w=0.75$ can be observed, which corresponds to the saturated solution part of the salt isotherms. In water activities above 0.75, the water content increases when the NaCl content increases. However, at lower water activities (below a_w 0.75) there is only a slight effect of NaCl content in the opposite direction, which can be explained by the increase of weight due to the addition of NaCl. A similar effect of NaCl above a_w 0.75 has been found by other authors in meat experiments (Lioutas et al., 1984) and also with other foodstuff and solutes (Bussiere and Serpelloni, 1985; Curme et al., 1990). The NaCl solution crystallizes below a water activity of 0.75 (its saturation point), so, below this value the crystallized NaCl absorbs little or no water. Above its saturation point the NaCl binds to water, and consequently at high water activities (above 0.75) the meat water content in equilibrium would be modified. This could explain why there is a breaking point in the isotherm at a water activity of 0.75.

The desorption isotherm could be divided into two parts, below and above this point. However, at temperature of 5 and 13°C points at $a_w=0.708$ is still in the high moisture content range. This effect can be explained by two hypotheses. The first one is that the water phase of the meat becomes a supersaturated NaCl solution during desorption. The second one is that the samples could not reach equilibrium. In fact, the difficulty of reaching a thermodynamic equilibrium in other food systems has been stated by other authors (Mannheim *et al.*, 1994). Motarjemi (1988) also had problems in the measurement of the sorption isotherm of lard at 60°C in which, after four months, the samples did not reach the equilibrium.

During the drying process of meat products, the relative humidity of the air often ranges from 60% to 80%. Therefore, one has to bear in mind that around water activities of 0.75 there would be a significant decrease in water content on the product surface with a slight decrease of relative air humidity (RH). In dry-cured hams this decrease would be more significant just after salting because at this point the NaCl content on the surface reaches its maximum, and this could lead to salt crystallisation when RH is less than 0.75. For instance, Arnau et al. (1995) found that the *Gracilis* muscle, which is an external muscle, achieved a NaCl content of 28.2% (d.m.) just after salting.

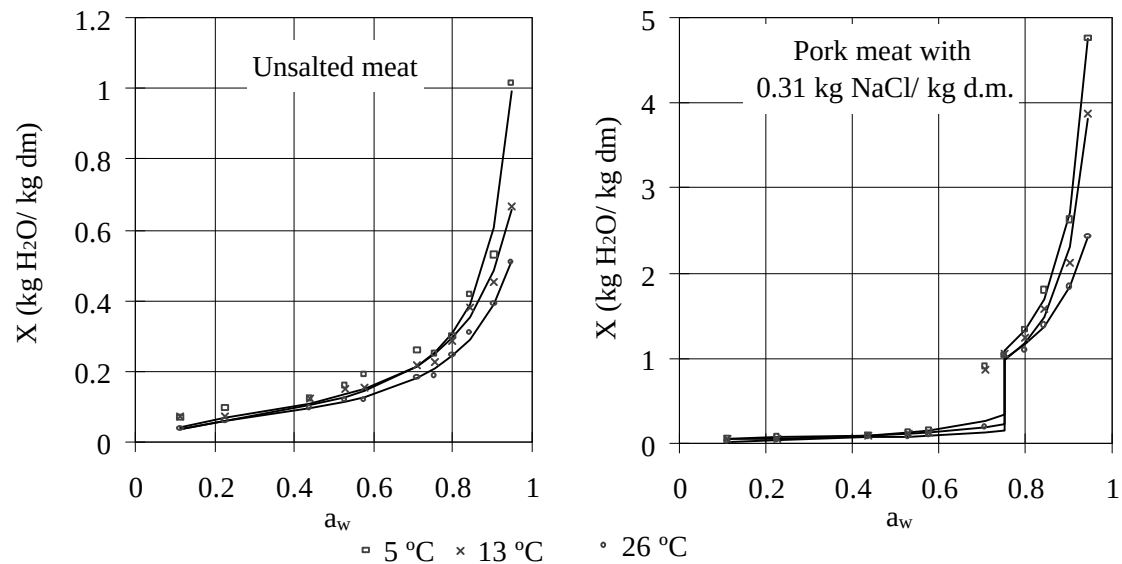


Figure 4.1.4 Calculated (—) and experimental (!, x, O) desorption isotherms at different temperatures for unsalted meat and salted meat 0.31 kg NaCl/ kg d.m. (model type 2). X: water content (kg H₂O/kg d.m.). (O): meat 26° C. (x) meat 13 °C. (!) meat 5 °C.

The temperature effect on desorption isotherms of unsalted meat is shown in Figure 4.1.4. The water content at a given water activity increases as temperature decreases, and this increase is higher at higher water activity. The same effect was observed with salted meat (Figure 4.1.4). This is shown in Table 4.1.1 where the interaction between temperature and NaCl content at $a_w=0.903$ becomes significant.

Table 4.1.1 Signification of the temperature and NaCl content effects, and its interaction on water content, at $a_w>0.75$.

	Temperature effect	NaCl content effect	Interaction (Temp*NaCl)
0.750	NS	***	NS
0.800	**	***	NS
0.843	***	***	NS
0.903	***	***	***
0.946	***	***	**

NS: not significant. **: $p<0.01$. ***: $p<0.001$.

At $a_w < 0.70$ there is a significative effect of temperature on water content. The NaCl content has a non significative effect at those a_w if the results are expressed as dry matter free of NaCl, and Temp*NaCl has neither a significative effect.

Water content in saturated NaCl solutions (a_w 0.75) is hardly depending on temperature within the range of temperatures used in this study (Chirife and Resnik, 1984). This can explain the non significative effect of temperature on water content in salted meat at a_w of 0.75 (Table 4.1.1).

The effect of applying high temperatures during the drying of meat products would be different if it were done in the first steps of the process (as it is in fermented sausages), when the products have a higher a_w , or if it is done in the last stages when the a_w is lower (as in dry cured hams).

If the a_w on the surface is high, an increase in temperature would produce an important decrease in the water content and this would accelerate the drying of the inner zones of the product. Moreover, if the a_w is low, the same increase of temperature would produce only a slight decrease in the surface water content. Therefore, in the dry cured-ham process, earlier application of high temperature if the product is safe from a microbiological point of view, may be of interest when energy consumption is being considered.

The experimental data has been fitted to different models. In the empirical models, the isotherms were divided in two parts (from 0.11 to 0.57 and from 0.75 to 0.94), and the data obtained at a water activity level of 0.70 has not been included in the model to avoid fitting problems at different temperatures. The predictive methods for solid mixtures were not divided.

4.1.1. Theoretical and empirical sorption isotherm models applied to meat

4.1.1.1. Model type I. Isotherm equation considering the effect of temperature and NaCl content by means of coefficients

The parameters obtained for each isotherm equation are given in Table 4.1.2 and Table 4.1.3.

Table 4.1.2 Parameters obtained for BET and GAB models for salted meat

	BET		GAB 1		GAB 2	
	$a_w < 0.75$	$a_w \geq 0.75$	$a_w < 0.75$	$a_w \geq 0.75$	$a_w < 0.75$	$a_w \geq 0.75$
a_1	11739.4	11748.43	8.62E-04	7.78E-04	-0.0014	0.0020
a_2	8.00E-08	40.140	3.68E-04	5.5360	-8.7E-05	0.0032
b_1	5.17E-04	2.57E-04	10501.5	10532.7	0.4670	-0.5144
b_2	-3.92E-04	3.85E-03	-0.1432	-193.41	-0.0346	-0.2661
c_1	1999.99	2000.31	23.442	13.435	1279.3	1279.3
c_2	5.67E-07	1.38E-01	-21.620	249.01	-4.2E-06	7.1E-05
d_1	14.280	64.840	21.000	21.025	-0.9264	-0.9719
d_2	-1.25E-06	4.98	-0.1581	0.9881	-0.0011	0.0173
e_1			0.6178	0.5692	0.0036	-0.0078
e_2			-0.0112	0.3620	5.13E-04	0.0125
f_1			1193.6	1285.7	-1.00	2.1759
f_2			-0.1209	-1327.2	1.88E-04	-3.4906
R^2	0.975		0.990		0.993	

Table 4.1.3 Parameters of Oswin, modified Halsey equation and Mujica equation for salted meat

	Oswin		Mujica <i>et al.</i> , 1989		Modified Halsey	
	$a_w < 0.75$	$a_w \geq 0.75$	$a_w < 0.75$	$a_w \geq 0.75$	$a_w < 0.75$	$a_w \geq 0.75$
a_1	-0.0817	0.1029	-1.2176	19.557	1.4982	0.9511
a_2	0.1732	3.3187	12.174	-6.2144	-0.7206	1.0513
b_1	-0.0008	0.0355	-0.0943	0.4733	-0.0291	-0.0329
b_2	-0.0024	-0.0005	0.3491	-0.1620	0.0081	0.0038
c_1	0.0029	0.1995	1.1990	19.883	-2.9288	-2.597
c_2	0.4031	0.9493	13.432	-6.2163	0.2503	5.6461
d_1	0.0072	-0.0049	-0.1588	0.5402		
d_2	0.0014	-0.0185	0.4052	-0.1913		
R^2	0.990		0.993		0.983	

The GAB 2 and Mujica *et al.* (1989) models gave the best fit, although the R^2 obtained for the rest of the models is still high. Other models were also used (Henderson model), but they could not fit well to the experimental data.

4.1.1.2. Model type II. GAB and Mujica models considering the effect of NaCl content by means of coefficients and considering the effect of temperature using Clausius-Clayperon equation

- Temperature effect

To be able to use the Clausius-Clapeyron equation, the equations of Table 3.1.2 must be expressed in terms of water activity depending on moisture content. GAB and Mujica equations (Table 3.1.2) were therefore rewritten in the following manner:

$$a_w = \frac{\frac{X}{X_{m,s}}(2 - C_{G,s}) + C_{G,s} - \sqrt{\left(\frac{X}{X_{m,s}}C_{G,s} - C_{G,s}\right)^2 + 4\frac{X}{X_{m,s}}C_{G,s}}}{2K_s \frac{X_s}{X_{m,s}}(1 - C_{G,s})} \quad 4.1.1$$

and

$$a_w = \frac{m_s - \frac{1}{X}}{n_s} \quad 4.1.2$$

The GAB equation was selected to describe a_w in $a_w < 0.75$ range and the empirical Mujica equation in the range $a_w \geq 0.75$.

The heat of sorption (Q_s) necessary in the model was determined on the basis of equation 3.1.3. The experimental measurements of desorption isotherm at different temperatures were plotted as $\ln a_w$ versus $1/T$ at different water contents (Figure 4.1.5). The slope of each straight line is $-Q_s/R$, therefore, a different heat of sorption was obtained for each different water content (Table 4.1.4). The Q_s was obtained by different NaCl content of the meat samples.

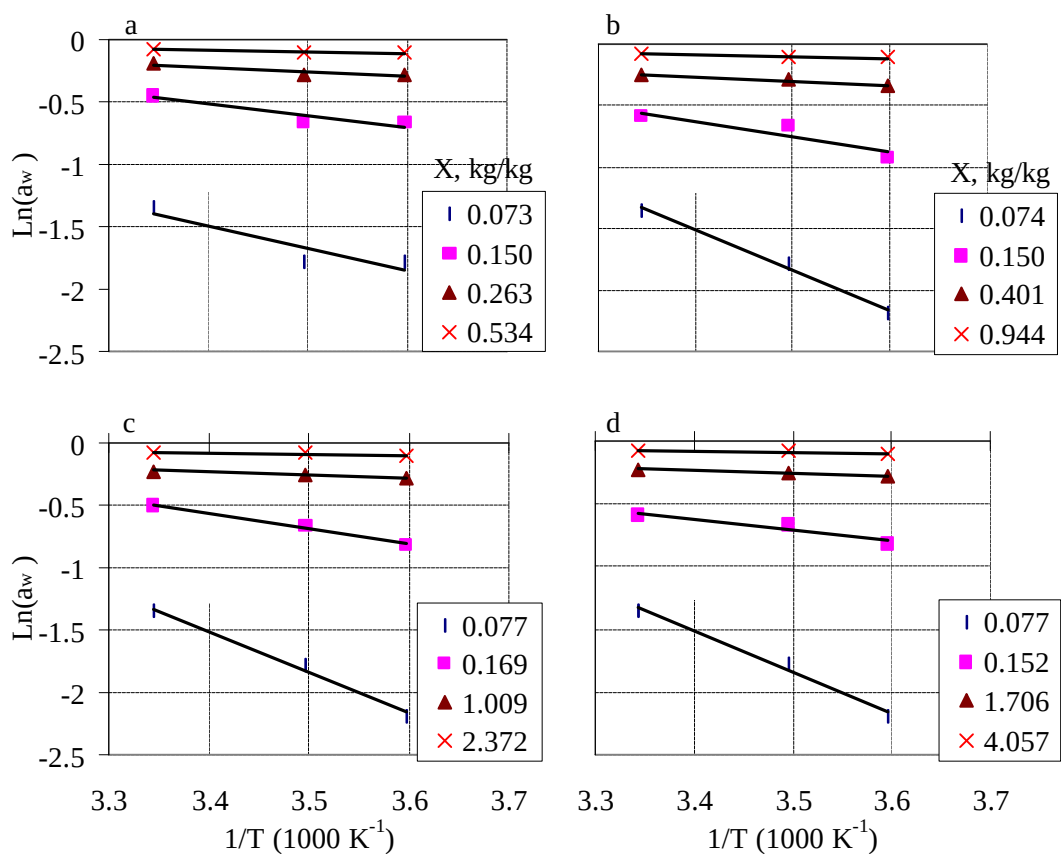


Figure 4.1.5 $\ln(a_w)$ versus $1/T$ at different moisture contents and at different NaCl contents in meat:
a: 0, b: 0.08, c: 0.20, d: 0.31 kg NaCl/kg d.m.

Table 4.1.4 Average water sorption heat values for meat at different water and NaCl content

NaCl content (kg NaCl/kg d.m.)	Water Content (kg H ₂ O/kg d.m.)	Average Q _s (J/mol)
0.00	0.073	14754.3
	0.150	7649.5
	0.263	2987.4
	0.534	1033.9
0.08	0.068	27203.4
	0.137	10294.5
	0.365	2839.7
	0.860	1033.9
0.20	0.061	27203.4
	0.133	10158.0
	0.797	1881.7
	1.873	902.5
0.31	0.052	27203.4
	0.102	7061.9
	1.149	1881.7
	2.732	902.5

The values of Q_s obtained are of the same order as the results reported in literature (Okos *et al.* 1992). For instance, he reported 10234 J/mol in raw beef at a water content of 0.15 kg/kg d.m.

A plot of heat of sorption Q_s dependence on moisture content is shown in Figure 4.1.6.

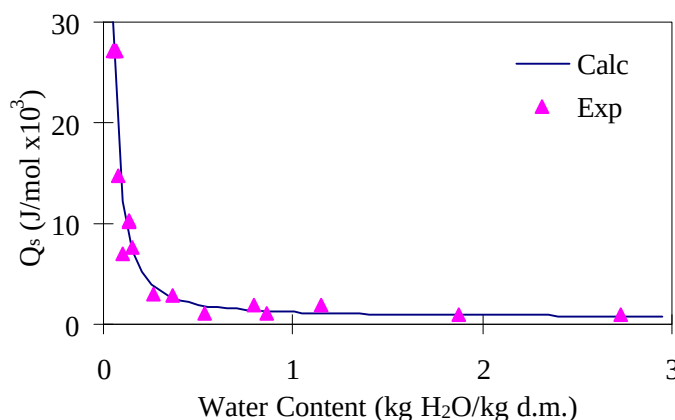


Figure 4.1.6 Plot of heat of sorption versus water content for raw and salted meat

The heat of sorption is then related to the water content using the following empirical equation:

$$Q_s = E_0 + \frac{1}{cX^d} \quad 4.1.3$$

Equation (4.1.3) is fitted to all experimental heat of sorption data versus water content of meat. By minimising the total sum of squared deviations between the experimental and calculated data the equation constants obtained are $c = 0.0021$, $d = 1.3921$ and $E_0 = 727.6$. E_0 is an empirical equation parameter that would correspond to the heat of sorption of pure water when the water content of the meat is very high. Motarjemi (1988) reports from other authors that the average energy to maintain the tetrahedral structure of the water molecule is about 20500 J/mol.

- NaCl effect

The effect of the NaCl content is included in the model as a linear relationship between the heat of sorption and the coefficients of the models.

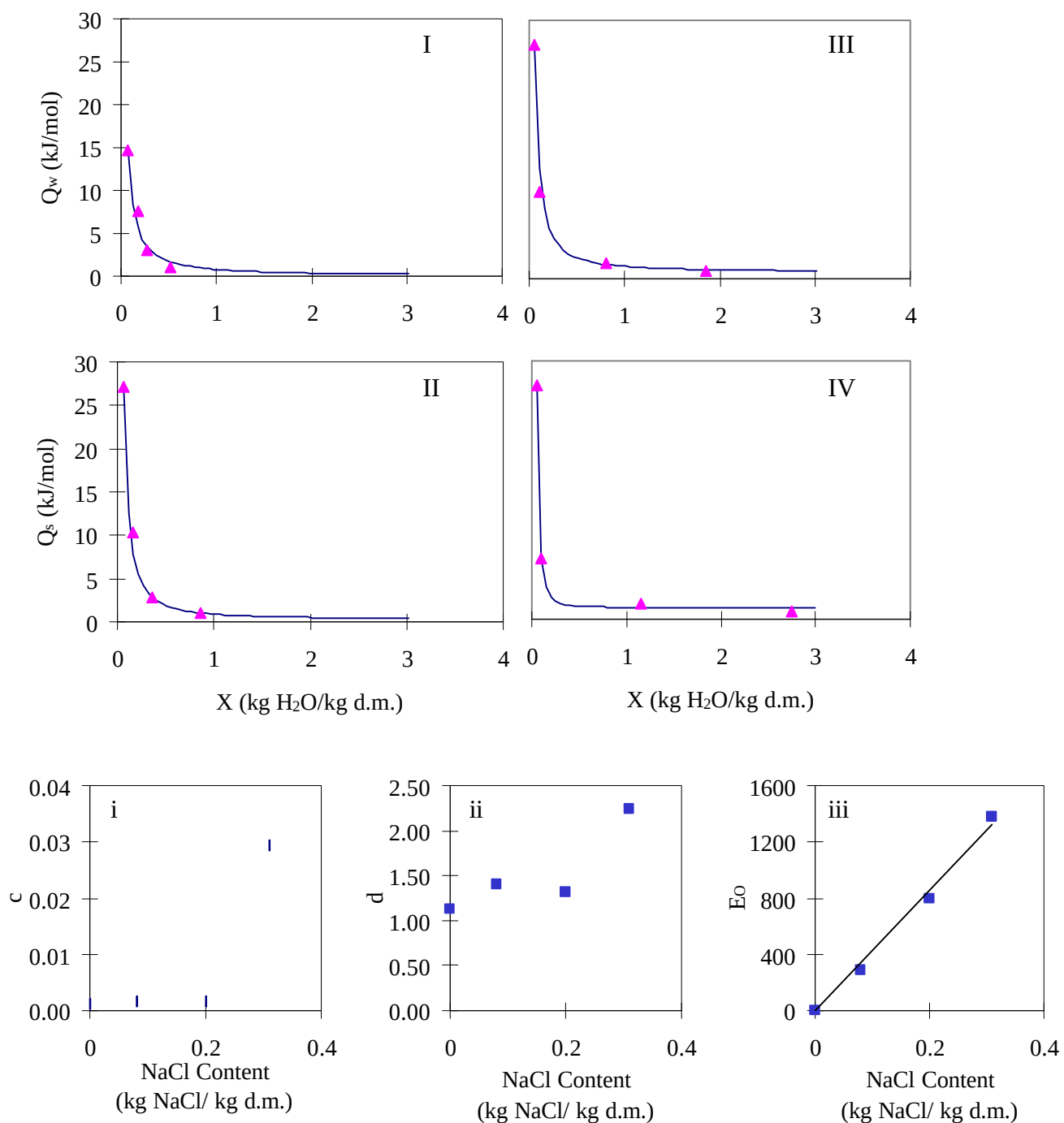


Figure 4.1.7 Heat of sorption of meat at different water content and different NaCl content. I: 0; II: 0.09; III: 0.23; IV: 0.31 kg NaCl / kg d.m. i: parameter c versus NaCl; ii: parameter d versus NaCl; iii: parameter E_0 versus NaCl. (—) calculated.

The relationship of the heat of sorption with the different NaCl content of the samples is obtained by plotting and fitting the equation (4.1.3) to the Q_s obtained for each NaCl content

(I, II, III, IV from Figure 4.1.7), from which, the obtained equation constants (c, d, E₀) are plotted against the NaCl content (i, ii, iii from Figure 4.1.7).

Figure 4.1.7 shows that only E₀ has a clear linear relationship versus NaCl content, while c and d seem not to be very much dependent on NaCl content, except for 0.31 kg NaCl/kg d.m. No explanation is obtained for this behaviour, therefore from these three parameters, only E₀ is included to the equation to model the effect of NaCl (equation 4.1.4). This relationship allows to observe that the E₀ increases when NaCl content increases, and so it may mean that more energy is required to move the water molecules. As it was explained previously (section 1.4), the relative strength of water-ions bonds is higher than in water-dipole. An effect of this behaviour could be observed in dilutions of NaCl and water, in which when NaCl concentration increases, the partial vapor pressure decreases (Rödel 1989).

The heat of sorption is related linearly to the NaCl content by the E₀ term through the equation 4.1.4. The coefficients e₁ and e₂ are shown in Table 4.1.5.

$$E_0 = e_1 \cdot w_s + e_2 \tag{4.1.4}$$

GAB and Mujica models are fitted to the experimental data for each temperature and each NaCl content, and the obtained parameters are plotted versus NaCl content (Figure 4.1.8). These plots allow to observe the relationship of the different parameters with the NaCl. A clear effect of NaCl is obtained for Mujica parameters (m_s, n_s), which is fitted to a polynomial equation (equations 4.1.8 and 4.1.9). Smaller dependence of NaCl is obtained using GAB parameters, which are considered to be linear dependent (equations 4.1.5 to 4.1.7). The values of the parameters of these equations are shown in Table 4.1.5.

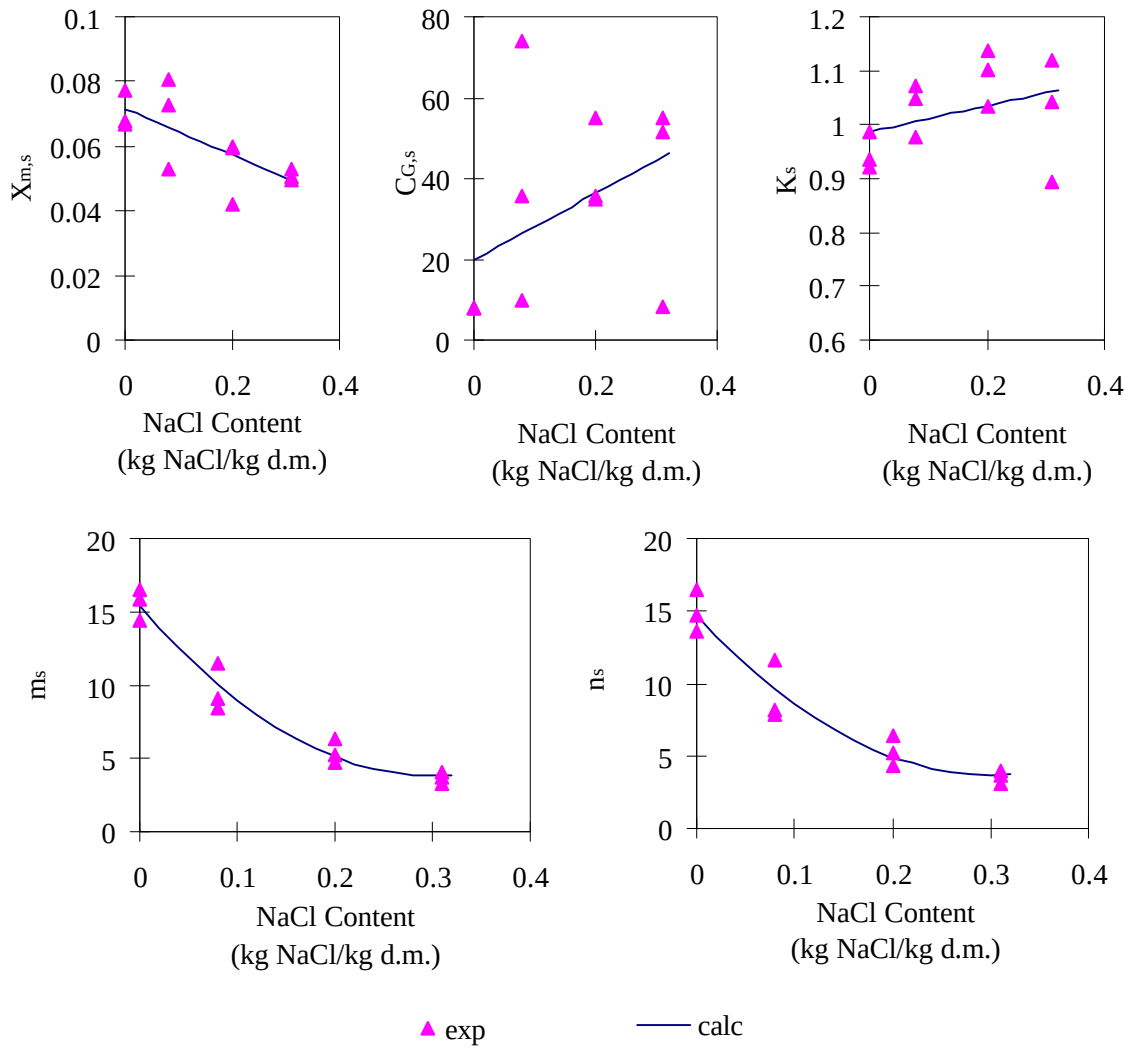


Figure 4.1.8 Isotherm equation constants versus NaCl content, for constants depending on salt content only. $X_{m,s}$, $C_{G,s}$, K_s :GAB model. m_s , n_s : Mujica model.

The parameters are fitted as it is shown in the following equations:

Using GAB parameters:

$$X_{m,s} = X_{m1} \cdot w_s + X_{m2} \quad 4.1.5$$

$$C_{G,s} = c_1 \cdot w_s + c_2 \quad 4.1.6$$

$$K_s = k_1 \cdot w_s + k_2 \quad 4.1.7$$

Using parameters of the Mujica equation (Mujica *et al.* 1989):

$$m_s = m_1 \cdot w_s^2 + m_2 \cdot w_s + m_3 \quad 4.1.8$$

$$n_s = n_1 \cdot w_s^2 + n_2 \cdot w_s + n_3 \quad 4.1.9$$

Table 4.1.5 Parameters obtained for GAB and Mujica models using the Clausius-Clapeyron equation

GAB		Mujica		Sorption heat coefficients	
$a_w < 0.75$		$a_w \geq 0.75$			
x_{m1}	-0.071	m_1	128.88	c	0.0021
x_{m2}	0.0715	m_2	-77.42	d	1.3921
c_1	82.14	m_3	15.415	e_1	4260.9
c_2	19.893	n_1	122.71	e_2	0.0205
k_1	0.2437	n_2	-73.556	T_{ref}	273+13
k_2	0.9864	n_3	14.72		
		R^2	=	0.998	

By rearranging the above expressions, it is possible to obtain an equation that relates water activity and the water content of meat at different temperatures and NaCl contents of meat. The analysis is shown below.

From equations (4.1.1) and (4.1.2) where a_w is related to the water content of the meat in the following form

$$a_w = f_1(X) \quad 4.1.10$$

and from the equation (3.1.3) where a_w is related to temperature in the form

$$a_w = f_2(T) \quad 4.1.11$$

by expressing equation (3.1.3) in terms of the actual and reference point one obtains

$$\ln \frac{a_w}{a_{w \text{ ref}}} = \frac{Q_s}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \quad 4.1.12$$

Substituting $a_{w \text{ ref}}$ with equation (4.1.10) yields

$$\ln \frac{a_{w2}}{f_1(X)} = \frac{Q_s}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad 4.1.13$$

and finally

$$a_w = f_1(X) \exp \left[\frac{Q_s}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right] \quad 4.1.14$$

Introducing $f_1(X)$ defined by equation (3.1.3) and (4.1.1), and also expressing Q_s by equation (4.1.3) as the final result one obtains:

$$a_w = \frac{\frac{X}{X_{m,s}} (2 - C_{G,s}) + C_{G,s} - \sqrt{\left(\frac{X}{X_{m,s}} C_{G,s} - C_{G,s} \right)^2 + 4 \frac{X}{X_{m,s}} C_{G,s}}}{2K_s \frac{X}{X_{m,s}} (1 - C_{G,s})} \exp \left[\frac{E_0 + \frac{1}{cX^d}}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right] \quad 4.1.15$$

and

$$a_w = \frac{m_s - \frac{1}{X}}{n_s} \exp \left[\frac{E_0 + \frac{1}{cX^d}}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right] \quad 4.1.16$$

where T_{ref} is the reference temperature, and T is the temperature at which the a_w is to be known.

From the above results, the equation (4.1.15) and the equation (4.1.16) are selected as providing the best fit. They are plotted in Figures 4.1.1, 4.1.2, 4.1.3 in comparison to the experimental results.

One must be aware of the fact that the equation (4.1.15) is applicable for a_w from 0.1 to 0.75, and the equation (4.1.16) from 0.75 to 0.94.

The R^2 obtained using this model (type II) is slightly higher than the previous empirical model (model type I). Therefore, the application of Clausius-Clapeyron equation improve a little the fitting. All the fits obtained using this empirical models can be considered to describe accurately the experimental data.

4.1.2. Predictive methods for solid mixtures

Theoretical isotherms for mixtures of unsalted meat and NaCl are calculated using the different predictive methods (seccion 3.1.6.2). This states that at any water activity, the expected moisture content of the mixture is equal to a mathematical relationship of the water sorbed by the individual components.

Sorption isotherm for salt (NaCl) has the typical form for soluble solids (Figure 4.1.9). It is composed of a solid sorption section ($a_w < 0.75$), saturated solution section ($a_w = 0.75$) and diluted solution section ($a_w \geq 0.75$). The threshold value of 0.75 should be considered approximate, as it varies from 0.7525 to 0.7565 in the range of temperature studied (5 to 26 °C) according to data of Greenspan (1977). The sorption isotherm of salt was described using the following equations:

- solid sorption – a straight line equation fitted to data of Leiras and Iglesias (1991). The data is available at room temperature only.

$$a_w = 98.92 \cdot X + 0.143 \quad 4.1.17$$

- saturated solution - a polynomial representing the relationship of the saturated solution a_w on temperature (from 0 to 80°C) was available in Greenspan (1977) and it has the following form:

$$a_w = 2.848 \cdot 10^{-7} t^3 - 2.65459 \cdot 10^{-5} t^2 + 3.98321 \cdot 10^{-4} t + 0.755164 \quad 4.1.18$$

- diluted solution – the modified Norrish equation is fitted to data of Chirife and Resnick, 1984. This section is very little dependent on temperature and the equation is valid in the range 15 to 50°C.

$$\ln a_w = -5.936 \left(\frac{1}{1+X} \right)^2 - 0.0143 \quad 4.1.19$$

The NaCl sorption isotherm synthesized from these parts is shown in Figure 4.1.9 as a dashed line.

The sorption isotherms of raw (unsalted) meat are measured in this work at three different temperatures (5, 13 and 26 °C). The GAB 2 equation is fitted to the experimental points. The estimated GAB constants are the following:

$$\begin{aligned} X_m &= -0.00167T + 0.5484 \\ C_G &= \exp\left(\frac{1279.3}{T} - 0.9195\right) \\ K &= \exp(-0.00359T + 0.0592) \end{aligned} \quad 4.1.20$$

The parameters gave a good fit ($R^2 = 0.986$) for experimental points at the temperature range used in this experiment. This sorption isotherm is shown in Figure 4.1.9 with dash and a dotted line.

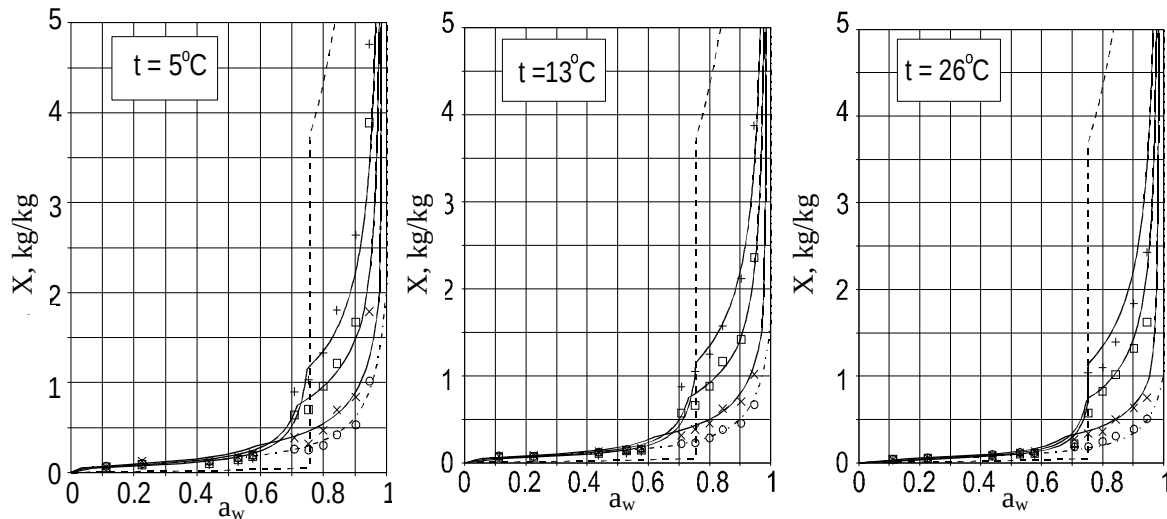


Figure 4.1.9 Prediction of a_w using Ross' method. (---) NaCl isotherm. (-.-) Raw meat isotherm. (—) Calculated isotherm. Experimental points: o: 0, x: 0.08, !: 0.20, +: 0.31 kg NaCl/kg d.m.

- Predictive methods

The above relationships were necessary to predict water activity of salted meat by the linear mixing rule and by the Ross's method.

The Lang and Steinberg method, which was applied in the range of $a_w > 0.75$ the following Smith isotherms (Smith, 1947) were fitted

$$X = a \log_{10}(1 - a_w) + b \quad 4.1.21$$

where:

		a	b
NaCl:	15-50 °C	-12.5857	-5.1118
Meat:	5 °C	-0.668	-0.0569
	13 °C	-0.471	-0.00429
	26 °C	-0.386	-0.00591

The exemplary sorption isotherms predicted by the three methods applied are shown at 13°C in Figure 4.1.10

The comparison indicates that Ross's method provides the best fit in the range of $a_w > 0.75$. The linear mixing rule reproduces well the drop of X_{mix} that occurs around $a_w = 0.75$ and the data for a_w below this point, but it consistently underestimates a_w in the $a_w > 0.75$ range. The

isotherm produced by the Lang and Steinberg method has smaller curvature than the observed experimental points and on the average doesn't reproduce the experimental points well.

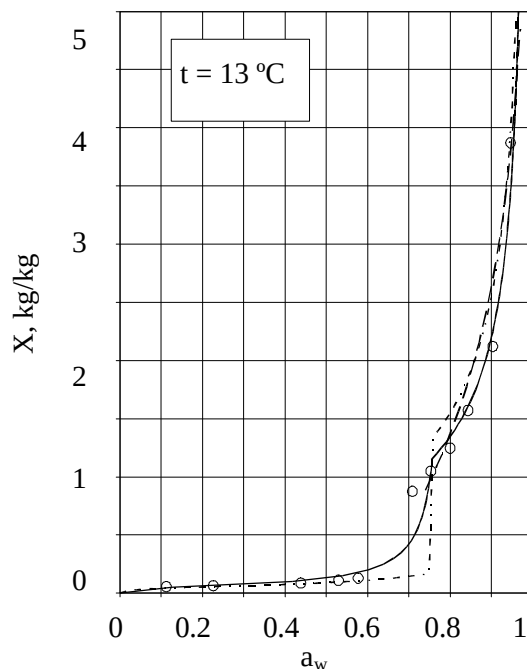


Figure 4.1.10 Prediction of a_w using different mixing rules: (—) Ross's method. (- - -) Linear mixing rule. (- · - ·) Lang and Steinberg method. (°) Experimental points: 0.31 kg NaCl/kg d.m.

The difference between the experimental data and the theoretical data for linear mixing rule could be due to the interaction between the NaCl and the meat, which would reduce the NaCl amount available to absorb water.

Sorption isotherms predicted by the Ross's method at all temperatures studied are shown in Figure 4.1.9. Coefficient of determination (R^2) of the model is 0.942. The results of prediction of a_w in the range 0.577 and 0.708 cannot be estimated as there are no experimental points available in this range. At high a_w this method deviates strongly from the experimental points. This result is in concordance to the fact that at high water activities the interaction of temperature and NaCl content is significative (Table 4.1.1), and an addition point is that the a_w of the NaCl dilution could be affected by the low temperatures (5 °C).

The methods of Salwin and Slawson and Chuang and Toledo were found not to be applicable to the present case. It can be anticipated that meat and NaCl mixture may exhibit departures

from the mixing rules due to the fact that salt is a strong electrolyte and may strongly interact with meat and its components.

The water content standard deviation and the residual errors versus a_w of Ross's method predictive fit and the equations obtained in section 4.1.1.1. and section 4.1.1.2. are shown in Table 4.1.8.

It is clearly visible that the empirical equations (GAB 2 from model type I and GAB/Mujica from model type II) provide better accuracy in the high range of a_w where Ross method deviates strongly from the experimental points.

At values below $a_w = 0.8$ the predictive Ross's method gives better accuracy than GAB 2 and GAB/Mujica. Therefore, to model drying kinetics in dry-cured ham, it is better to use Ross's method because the process of dry cured ham usually is developed at a relative humidity below 0.8. If the purpose is to obtain information about the microbiological stability of the meat, it is better to use the equations which do not use mixing rules for the range of a_w above 0.8. At this range the accuracy is slightly better.

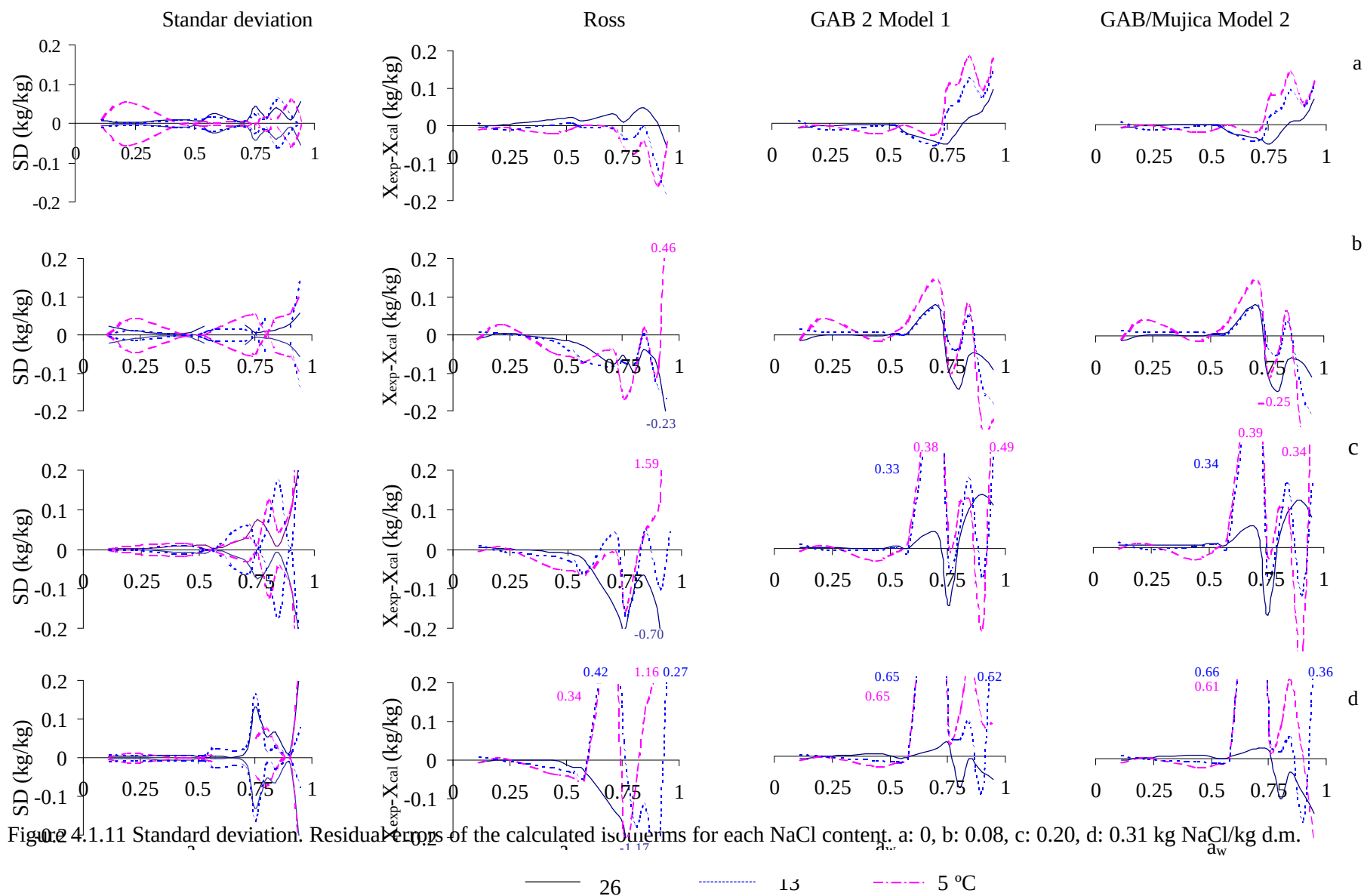


Figure 4.1.11 Standard deviation. Residual errors of the calculated isotherms for each NaCl content. a: 0, b: 0.08, c: 0.20, d: 0.31 kg NaCl/kg d.m.

