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WATER SORPTION PROPERTIES OF DUTCH TYPE SEMI-HARD CHEESE EDGE IN THE RANGE OF COMMON STORING TEMPERATURES

M. C. S. Pereira, J. Štencl, B. Janštová, V. Vlášek

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Abstract

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Moisture sorption isotherms of Dutch type semi-hard cheese edge in the temperature range of 10–25 °C and water activity (Aw) from 0.11 to 0.98 were determined using manometric method. The sorption curves had a sigmoid shape. The equilibrium moisture content (EMC) of cheese samples increased with an increase in Aw at a constant temperature both for water adsorption and desorption. An increase in temperature caused an increase in Aw for the same moisture content (MC) and, if Aw was kept constant, an increase in temperature caused a decrease in the amount of absorbed water. Critical values of equilibrium moisture content, corresponding to the Aw = 0.6, were between 11 % MC (w.b.) and 17 % MC (w.b.) both for moisture adsorption and desorption. Values of sorption heat were calculated from moisture sorption isotherms by applying the Clausius-Clapeyron equation. Values of the heat of desorption are higher than those of adsorption and the difference increases with the MC decrease. Heat of sorption decreased from 48.5 kJ/mol (~5.5 % MC w.b.) to the values approaching the heat of vaporization of pure water, free MC. The critical value for free water evaporation is about w = 27 % (w.b.) for the range of temperature 10–25 °C.

cheese, moisture content, sorption curve, sorption heat, water activity

The Dutch type semi-hard cheese is made in fairly large loaves of flat cylindrical shape from fresh un-skimmed milk. The mass is usually between 4 and 12 kg. The Dutch type varieties are one of the most important cheese produce in the world (Walstra *et al.*, 1993). Water sorption properties of the cheese edge part were tested, because this surface layer is in direct contact with the near ambient air during storage and moreover it creates a natural consumable package. Moisture content (MC) plays an important role in food quality; it influences texture and porosity, physical, chemical, and microbial properties. Water activity (Aw) values were measured from the viewpoint of the food safety (Beuchat, 1981), too. For a qualitative discussion of the sorption it is necessary to determine how sensitive the equilibrium moisture content (EMC) of the food is to temperature changes (Fontana and Campbell, 2004; Vitazek *et al.*, 2003; Labuza, 1984). These equilibrium data are used to predict storage stability and package conditions, too. Moisture sorption isotherms (MSI) show the equilibrium relationship between Aw and EMC (w_e) of wet material at a constant temperature and pressure (Rao and Rizvi, 1995). Thus, with knowledge of the MSI, it is possible to predict the maximum moisture that the food can be allowed to gain during the storage under precisely defined ambient air conditions. The temperature dependence of Aw is usually evaluated using a thermodynamic parameter heat of sorption (q^{st}) and Clausius-Clapeyron equation (Delgado and Sun, 2002). This equation can be expressed as follows:

$$\frac{d \ln \frac{p}{p_0}}{dT} = \frac{d \ln a_w}{dT} = \frac{q^{st}}{RT^2} \qquad (1)$$

or

$$\ln a_w = -\left(\frac{q^{st}}{R}\right)\frac{1}{T} + K, \tag{2}$$

where

p .... vapour pressure of water in a biological material,

p_0 ... saturated water vapour pressure,

T.... temperature in K,

R.... the universal gas constant (8.314 J/mol K).

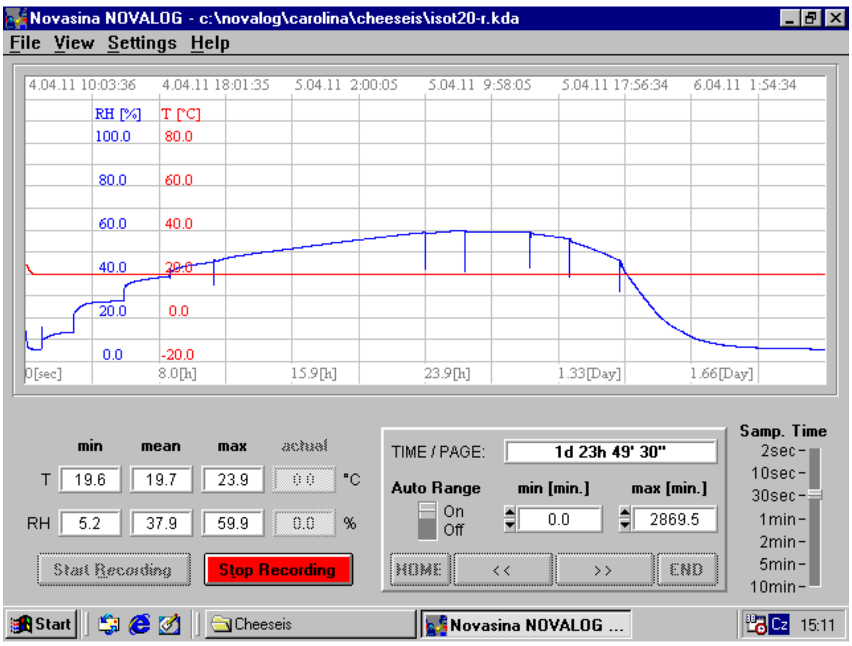
Aims of the presenting work were as follows: Aw measurements of the semi-hard cheese edge under storing temperatures, MC determination of samples tested, MSI creation and mathematical modeling, determination of q_n^{st} with the purpose to evaluate free MC and bounded MC, and finally to make analysis of water sorption properties of the cheese surface layer from the viewpoint of the food safety.

MATERIAL AND METHODS

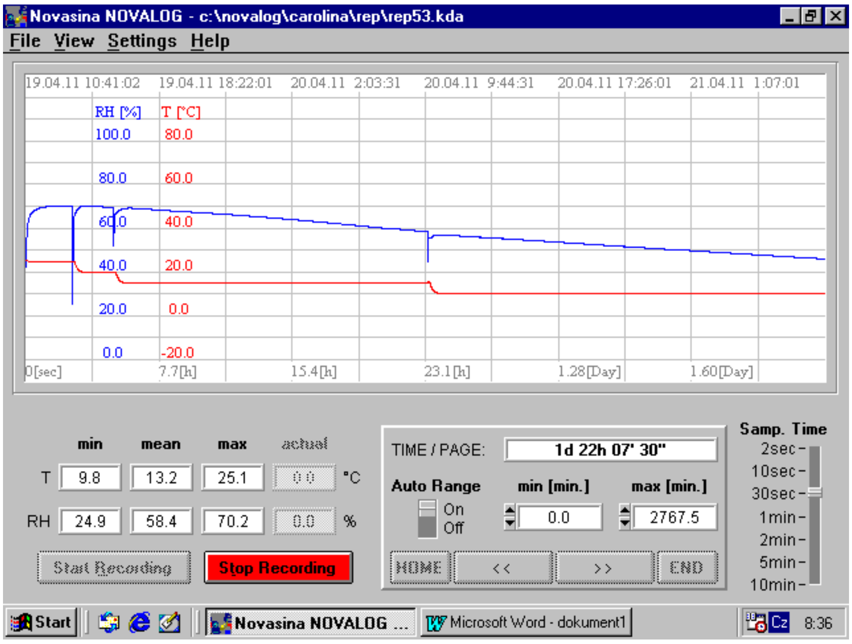
Dutch type semi-hard cheese was commercial produced and it was purchased in the market. Edge samples were randomly chosen and stored before measurements in the fridge under temperature 7 °C. The initial dry matter (DM) was about 88% and fat in DM was 45.2%. The average weight of samples was 1.283 g, the maximum and minimum value were 1.43 g and 1.036 g, respectively. The manometric static method (Iglesias and Chirife, 1982) was used for sorption tests in the temperature regime 10, 15, 20 and 25 °C. EMC of cheese samples, both for water adsorption and desorption, were determined in the range of relative air humidity (RH) between 11.3 and 98%. Six humidity salts were used for sorption tests: LiCl for RH 11.3%, $MgCl_2$ for RH 33%, $Mg(NO_3)_2$ for RH 53%, NaCl for RH 75.3%, $BaCl_2$ for 90%, and $K_2Cr_2O_7$ for 98%. The apparatus was calibrated with the above mentioned salts before the water sorption measurements of the cheese. The procedure of each test was as follows: after reaching the EMC of each sample at certain relative air humidity and constant temperature, the relative air humidity (corresponding salt) was changed; with increasing RH for water adsorption and with decreasing RH for water desorption, see an example on Fig. 1.

These EMC results were checked by tests with changing temperature and constant humidity salt used, see an example on Fig. 2.

Each of the tests was repeated three times at least. MC of samples were determined gravimetrically with the use of halogen moisture analyzer. The experimental EMC data were processed and analyzed using the non-linear regression procedure of Maple. The q^{st} can be determined from calorimetric measurements or from moisture sorption data (Štencl *et al.*, 2010). The second method is more convenient, given that MSI's are determined routinely (Chen, 2006; Falade *et al.*, 2004). The usual procedure to evaluate the q^{st} consists of plotting the sorption isostre as Aw versus $1/T$ and determining the slope which is equal to q^{st}/R. There are numerous models predicting the relationship among EMC, Aw and temperature, e.g. Iglesias and Chirife (1976), Chen and Morey (1989). The Henderson equation has been used for delineation of cheese MSI's in the temperature regime 10–25 °C:



1: *Course of a sorption test for cheese sample carried out at constant temperature*



2: *Course of a sorption test for cheese sample carried out at decreasing temperature*

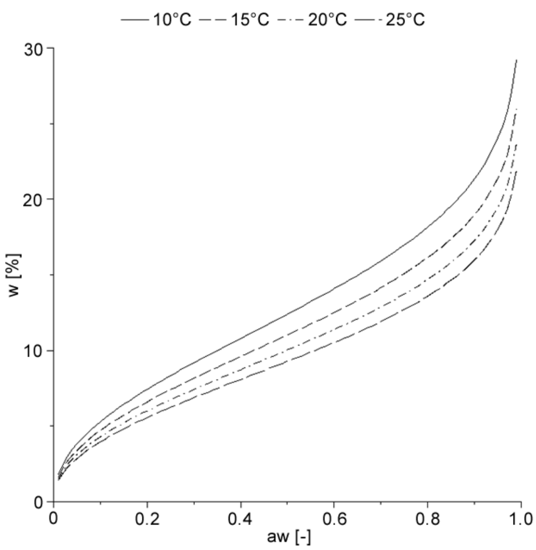
$$w_e = \left(\frac{\ln(1 - Aw)}{a(t + b)} \right)^c \qquad (3)$$

where
w_e .... EMC [% (w.b.)],
Aw [-]... water activity,
t .... temperature [°C],
a, b, c .... constants for the particular equation [-].

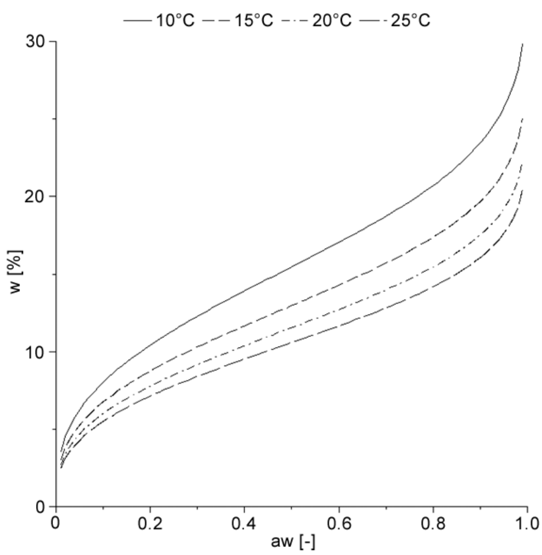
RESULTS AND DISCUSSION

The experimental adsorption and desorption isotherms for 10, 15, 20, and 25 °C are shown in Figs. 3 and 4.

In accordance with hypothesis, the sorption curves had a sigmoid shape. The EMC of cheese samples increased with an increase in Aw at a constant temperature both for water adsorption and desorption (Resio *et al.*, 1999). An increase in temperature caused an increase in Aw for the same MC and, if Aw was kept constant, an increase in temperature caused a decrease in the amount of absorbed water, see figures above. The EMC data

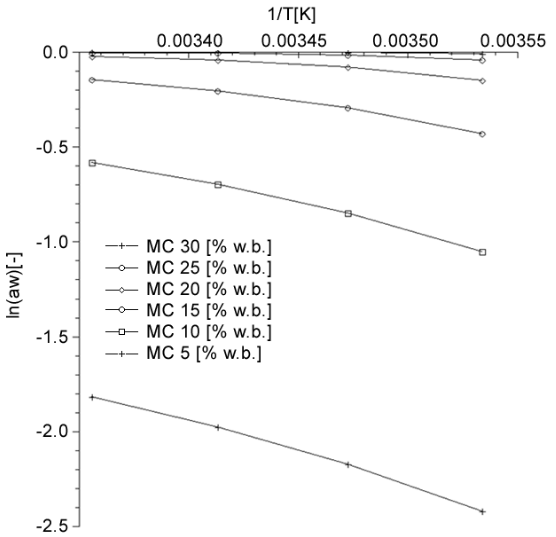


3: *Adsorption isotherms for Dutch type semi-hard cheese edge at 10, 15, 20, and 25 °C*

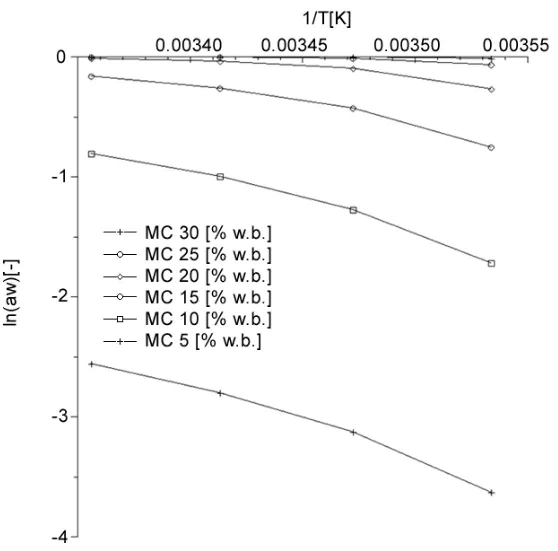


4: *Desorption isotherms for Dutch type semi-hard cheese edge at 10, 15, 20, and 25 °C* for q_n^{st} determination of the cheese in the Aw range of 0.11–0.98 were calculated using equation (3). Values of sorption heat were calculated from MSI's by applying the Clausius-Clapeyron equation (1) or (2). Figs. 5 and 6 show the plot of $ln(a_w)$ versus $1/T$ for cheese at MC from 5 to 30% (w.b.) for water adsorption and desorption, respectively, and since no significant dependence on temperature was observed, the modified Clausius-Clapeyron equation (4) was used to calculate the q^{st} (Jamali *et al.*, 2006; Delgado and Sun, 2002):

$$\frac{\ln a_{w_2} - \ln a_{w_1}}{T_2 - T_1} = \frac{q^{st}}{RT_1T_2}. \tag{4}$$

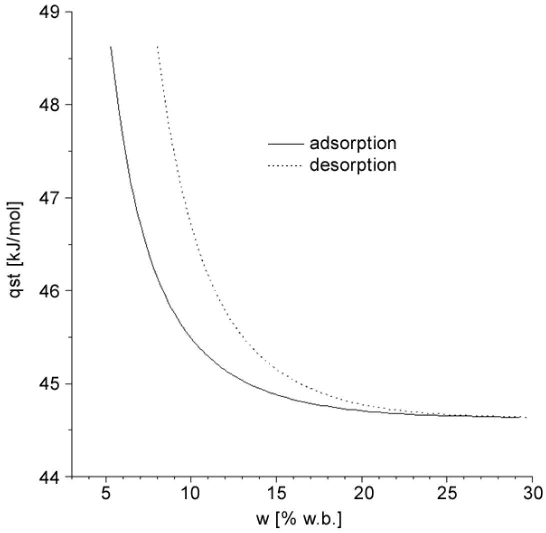


5: *Plot of ln(Aw) versus 1/T for Dutch type semi-hard cheese edge, moisture adsorption*



6: *Plot of ln(Aw) versus 1/T for Dutch type semi-hard cheese edge, moisture desorption*

Values of q^{st} at a specific MC give an indication of the state of sorbed water and a level of the physical, chemical and microbiological stability of the wet biological material under specific near ambient air conditions, too. The cheese q^{st} is indicated in the form of q^{st} versus MC in Fig. 7.



7: *Heat of sorption for Dutch type semi-hard cheese edge in the temperature range of 10–25 °C*

Values of the heat of desorption are higher than those of adsorption and the difference increases with the MC decrease. This indicates that the energy required in the drying process is greater than that in the moistening process (Jamali *et al.*, 2006; Delgado and Sun, 2002). The q^{st} values decreased from 48.5 kJ/mol (~5.5% MC w.b.) to the values approaching the heat of vaporization of pure water (Rao *et al.*, 2006). The level of moisture content at which the q^{st} approaches the heat of vaporization of water is indicative for free MC in the material (Iglesias and Chirife, 1976). The critical value for free water evaporation is about w = 27% (w.b.) for the range of temperature 10–25 °C.

CONCLUSIONS

The MSI's provide valuable information about the hygroscopic equilibrium of the Dutch type semi-hard cheese edge in the temperature range of 10 °C and 25 °C. Under constant Aw, the sorption capacity of the cheese decreased with increasing temperature. It indicated that the material bacame less hygroscopic at higher temperatures. Rehydration of the cheese resulted in hysteresis, see MSI curves for water desorption and adsorption. The Clausius-Clapeyron equation was used to calculate the q^{st} and its variation with MC. The q^{st} shows the temperature dependence of Aw. Values of the heat of desorption are higher than those of adsorption and the difference increases with the MC decrease. This indicates that the energy required in the drying process is greater than that in the moistening process.

The critical Aw also exists below which no microorganisms can grow (Beuchat, 1981). For most foodstuffs, this is in the range of 0.6–0.7 Aw. The presented MSIs show, that critical MC of tested cheese is between 11% MC (w.b.) and 17% MC (w.b.) from the point of view microbial proliferation.

SUMMARY

The paper deals with interactions between Dutch type semi-hard cheese edge and near ambient air. Edge samples were randomly chosen and stored before measurements in the fridge under temperature 7 °C. The initial dry matter (DM) was about 88% and fat in DM was 45.2%. The average weight of samples was 1.283 ± 0.1 g. The manometric static method was used for sorption tests in the temperature regime 10, 15, 20 and 25 °C. Equilibrium moisture content of cheese, both for water adsorption and desorption, was determined in the range of relative air humidity (RH) between 11.3 and 98%. The experimental data of sorption isotherms were processed and analyzed using the nonlinear regression. The sorption curves had a sigmoid shape. The EMC of cheese samples increased with an increase in Aw at a constant temperature both for water adsorption and desorption. An increase in temperature caused an increase in Aw for the same MC and, if Aw was kept constant, an increase in temperature caused a decrease in the amount of absorbed water. Critical values of equilibrium moisture content, corresponding to the Aw = 0.6, were between 11% MC (w.b.) and 17% MC (w.b.) both for moisture adsorption and desorption. Clausius-Clapeyron equation was used to calculate the heat of sorption and its variation with MC. Values of the heat of desorption are higher than those of adsorption and the difference increases with the MC decrease. Heat of sorption decreased from 48.5 kJ/mol (~5.5% MC w.b.) to the values approaching the heat of vaporization of pure water, free MC. The critical value for free water evaporation is about w = 27% (w.b.) for the range of temperature 10–25 °C.

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Address

MSC. M. C. S. Pereira, Escola Superior Agrária, Instituto Politénico de Coimbra, Portugal, doc. Ing. Jiří Štencl, DrSc., MSC. Maria Carolina Soares Pereira, Ústav zemědělské potravinářské a environmentální techniky, Mendelova univerzita v Brně, Zemědělská 1, 613 00 Brno, Česká republika, doc. MVDr. Bohumíra Janštová, Ph.D., Mgr. Václav Vlášek, Ústav hygieny a technologie mléka, Veterinární a farmaceutická univerzita Brno, Palackého 1/3, 612 42 Brno, Česká republika, e-mail: carolina_spereira@hotmail.com, stencl@mendelu.cz, ysoaresp@node.mendelu.cz, janstovab@vfu.cz, H10017@vfu.cz