Thermochimica Acta, 184 (1991) 313–319
Elsevier Science Publishers B.V., Amsterdam

Moisture adsorption behaviour of fish foodstuffs at different temperatures

M.J. Alcaraz, M.I. Paz Andrade and F. Sarmiento[1]

Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago,
15706 Santiago de Compostela (Spain)

(Received 12 November 1990)

Abstract

A new method for determining the water activity of biological products has been applied to determine the water activity of tuna (*Thunnus alalunga*) and hake (*Merluccius merluccius*) at different temperatures in different forms of preservation. The method is based on the equilibrium moisture adsorption of microcrystalline cellulose, whose isotherms at 278.15, 298.15 and 313.15 K were compared. The water content was reduced by increasing the temperature. Heats of sorption, obtained from the Clausius–Clapeyron equation, increased at first (water content less than 4 g per 100 g DM) but then decreased to the value of the heat of vaporisation of water.

INTRODUCTION

Water vapour sorption isotherms represent the sorption equilibrium at constant temperature between the vapour pressure of water in the gas phase and the moisture content of the material in question. Owing to the great range of materials, the methodology has always been characterised by an exceptional diversity of apparatus and methods. In recent years, considerable attention has been paid to the proper characterisation of materials and methods in reporting on sorption measurements [1,2]. Sorption isotherms are used extensively to study the water binding properties of foodstuffs, because the control of water activity in food processing is of major importance in relation to microbial spoilage and growth of pathogens, which are accelerated at higher water activities [3].

There is a strong correlation between water content and mechanical properties of biological materials: electrical conduction and microwave attenuation increase suddenly by around 75–80%, corresponding to the growing importance of water–water interactions in preference to the water–substrate interactions that predominate at lower humidities [4]. Sorption

---

[1] Author to whom correspondence should be addressed.

0040-6031/91/$03.50

data for several foods have been reported by Chen et al. [5], Wallingford and Labuza [6] and Cadden [7]. Adsorbed water can be partitioned into its "monolayer", "multilayer" and "condensed" forms and compared with the predictions of mathematical models such as the Guggenheim–Anderson–De Boer (GAB) equation [8]; the energy required for the sorption process can be calculated and the curve of heat of sorption versus water content obtained.

The purpose of this study was to investigate the effects of temperature on tuna (*Thunnus alalunga*) and hake (*Merluccius merluccius*) in different forms of preservation.

EXPERIMENTAL

Materials

Saturated solutions of LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, NaBr, $SrCl_2$, NaCl, KCl and $BaCl_2$ were used. Microcrystalline cellulose was purchased from Avicel Merk. Tuna (*Thunnus alalunga*) and hake (*Merluccius merluccius*) were used in different forms of preservation.

For practical sorption isotherm measurements, a device was constructed consisting of a rectangular thermostat (precision $\pm 0.01°C$), sorption containers and Petri dishes on trivets.

Method

The water activity of the food products was measured using the method of equilibrium moisture adsorption of microcrystalline cellulose (MCC). The MCC was dried in an oven for 24 hours at 100°C. Several 2 g samples (weighed to within < 0.0001 g) of the standard MCC were placed on a plate in a desiccator containing 50–100 g of the food sample. The desiccator was maintained at a given temperature (278.15, 298.15 or 313.15 K) for several days. After equilibrium had been reached, the lowest temperature sample taking longest to do so, the MCC was weighed and the moisture content was calculated from the weight gain.

The water activity of food products was determined by referring to the standard curve of water activity against moisture content for microcrystalline cellulose at equilibrium. These isotherms were found by measuring the adsorption isotherm of microcrystalline cellulose over saturated salt solutions using several samples to prepare the curve.

The isotherm data were fitted by the Guggenheim–Anderson–De Boer (GAB) model as outlined by Bizot [8]. The form of the equation used was

$$a_w/W = \alpha a_w^2 + \beta a_w + \gamma \qquad (1)$$

with

$$\alpha = \frac{k}{W_m}(1/C - 1) \tag{2}$$

$$\beta = \frac{1}{W_m}(1 - 2/C) \tag{3}$$

$$\gamma = \frac{1}{W_m Ck} \tag{4}$$

where a_w is the water activity, w is the water content of the sample on a dry weight basis, W_m is the water content corresponding to saturation of all primary adsorption sites by one water molecule (formerly called the monolayer in B.E.T. theory [9]) and C is the Guggenheim constant

$$C = C' \exp(H_1 - H_m)/RT \tag{5}$$

in which H_1 is the total heat of sorption of the first layer in primary sites, H_m is the total heat of sorption of the multilayer, which differs from the heat of condensation of pure water, and k is a correcting factor for properties of the multilayer molecules relative to the bulk liquid

$$k = k' \exp(H_m - H_e)/RT \tag{6}$$

where H_e is the heat of condensation of pure water vapour.

The quality of the fit of the GAB model was judged from the value of the relative percentage root-mean-square (%RMS)

$$\%\mathrm{RMS} = 100\left[\frac{\sum(W_i - W_i^*)^2}{N}\right]^{1/2} \tag{7}$$

where N is the number of experimental points, W_i is the average experimental water content and W_i^* is the calculated water content.

Heats of sorption, Q_s, the amount of energy required to remove water from the substrate in excess of the amount required for normal water vaporisation, were derived from the Clausius–Clapeyron equation [9]

$$\ln(a_2/a_1) = Q_s/R[(1/T_1) - (1/T_2)] \tag{8}$$

where a_2 is the water activity at temperature T_2, a_1 is the water activity at temperature T_1, Q_s is the isosteric heat of sorption (kJ per kg H_2O) and R is the gas constant (0.46188 kJ per kg H_2O).

RESULTS AND DISCUSSION

Table 1 shows the values of moisture adsorption of MCC as determined by the Guggenheim–Anderson–De Boer (GAB) model. The standard sorption isotherms at each temperature have the characteristic sigmoidal shape

TABLE 1

Moisture adsorption of microcrystalline cellulose as determined by the Guggenheim–Anderson–De Boer (GAB) model

	Temperature		
	278.15 K	298.15 K	313.15 K
α	-0.0897 ± 0.0034	-0.1311 ± 0.0009	0.1559 ± 0.0298
β	0.1359 ± 0.0386	0.1794 ± 0.0010	0.2129 ± 0.0286
γ	0.0248 ± 0.0094	0.0225 ± 0.0023	0.2708 ± 0.0060
GAB constants			
W_m	6.05	4.68	4.01
C	11.21	12.49	13.66
k	0.59	0.67	0.67

described by Mazza [10] and Van den Berg and Bruin [11] (Fig. 1). Each isotherm could be partitioned into an initial "multilayer region" (water activity levels less than 0.2), an intermediate "multilayer region" (water activity levels of 0.2–0.7) and a final "condensed water region" (water activity levels greater than 0.7). The moisture content of MCC decreased when the temperature was increased from 278.15 to 313.15 K.

Tuna and hake adsorbed similar amounts of water for the three temperatures studied (see Tables 2–4). However, the water content tended to be larger at 298.15 K than at 278.15 or 313.15 K. This may be due, in part, to solubility differences for different components at these temperatures. There

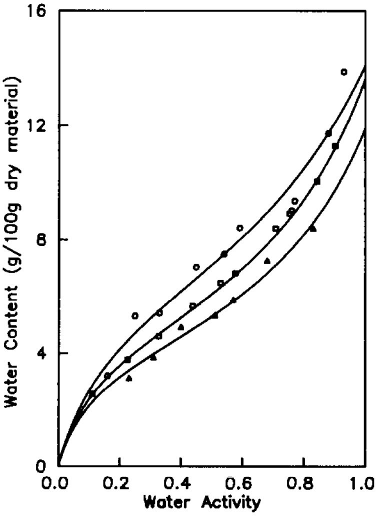

Fig. 1. Standard sorption isotherms for microcrystalline cellulose at (○) 278.15 K, (□) 298.15 K and (△) 313.15 K.

TABLE 2

Water activities and heats of sorption for tuna and hake in different forms of preservation at 278.15 K

	Water content (g per 100 g DM)	%RMS	a_w	Q_s (kJ K^{-1})
Tuna in brine	12.42	1.99	0.9180	750
Tuna in oil	12.26	1.49	0.9095	810
Tuna in pickled sauce	12.53	0.58	0.9240	720
Defrosted hake	13.23	1.50	0.9600	520
Fresh hake	13.26	6.60	0.9615	510

TABLE 3

Water activities and heats of sorption for tuna and hake in different forms of preservation at 298.15 K

	Water content (g per 100 g DM)	%RMS	a_w	Q_s (kJ K^{-1})
Tuna in brine	13.14	1.75	0.9830	550
Tuna in oil	13.00	6.50	0.9780	590
Tuna in pickled sauce	13.06	1.39	0.9800	570
Defrosted hake	12.82	1.84	0.9710	640
Fresh hake	13.33	3.01	0.9900	500

TABLE 4

Water activities and heats of sorption for tuna and hake in different forms of preservation at 313.15 K

	Water content (g per 100 g DM)	%RMS	a_w	Q_s (kJ K^{-1})
Tuna in brine	8.81	3.25	0.8435	3140
Tuna in oil	9.03	4.11	0.8580	3000
Tuna in pickled sauce	9.72	4.18	0.8990	2700
Defrosted hake	9.22	3.23	0.8650	2900
Fresh hake	9.15	5.25	0.8660	2900

are sufficient similarities in the data obtained from these and other systems to encourage the belief that the underlying sorption mechanisms have general applicability. Indeed, the similarities extend to synthetic polymers, as seen in the review by McLaren and Rowen [12].

Figure 2 shows the heats of sorption for MCC between two temperatures. Heats of sorption (Q_s) are differential quantities that vary inversely with the amount of water adsorbed by the solid [13]; at higher moisture contents, less energy is required to remove water molecules from the solid; that is, the

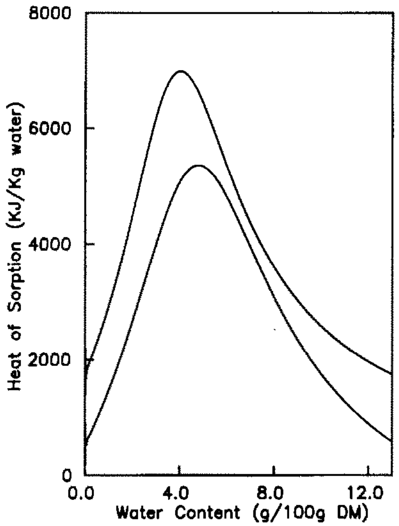

Fig. 2. Heats of sorption for microcrystalline cellulose between two temperatures: top, $T_1 = 298.15$ K and $T_2 = 313.15$ K; bottom, $T_1 = 278.15$ K and $T_2 = 298.15$ K.

water in the "monolayer region" is more tightly bound than that in the "condensed water regions" of the isotherm. Increasing the temperature from 278,15 to 298.15 K did not affect sorption data for tuna and hake.

ACKNOWLEDGEMENT

This work was supported by funds from Xunta de Galicia (grant XUGA 80408088).

REFERENCES

1 W. Wolf, W.E.L. Spiess and G. Jung, WasserdampfSorptionsisothermen von Labensmitteln. No. 18, Fachgemeinschaft Allgemeine Lufttechnik VDMA, Frankfurt am Main, 1973.
2 M.C. Gough and G.A. Bateman, Trop. Stored Prod. Inf., 33 (1977) 25.
3 P.T. Vos and T.P. Labuza, J. Agr. Food Chem., 22 (1974) 2.
4 I.C. Watt, in R. Jowitt, F. Escher, B. Hallström, H.F.Th. Meffert, W.E.L. Spiess and G. Vos (Eds.), Physical Properties of Foods, Applied Science Publishers, New York, 1983, p.3.
5 J.Y. Chen, M. Piva and T.P. Labuza, J. Food Sci., 49 (1984) 59.
6 L. Wallingford and T.P. Labuza, J. Food Sci., 48 (1983) 1.
7 A. Cadden, J. Food Sci., 53 (1988) 1150.
8 H. Bizot, in R. Jowitt, F. Escher, B. Hallström, H.F.Th. Meffert, W.E.L. Spiess and G. Vos (Eds.), Physical Properties of Foods, Applied Science Publishers, New York, 1983, p. 43.

9 S. Brunauer, P.H. Emmett and E. Teller, J. Am. Chem. Soc., 60 (1938) 309.
10 G. Maza, Am. Potato, 57 (1980) 91.
11 C. Van den Berg and S. Bruin, in L.B. Rockland and G.F. Stewart (Ed.), Water Activity: Influences on Food Quality, Academic Press, New York, 1981, p.1.
12 A.D. McLaren and J.W. Rowen, J. Polym. Sci., 7 (1951) 289.
13 T.P. Labuza, in Moisture Sorption: Practical Aspects of Isotherm Measurement and Use, American Association of Cereal Chemists, St. Paul, MN, 1984.