

Scientific paper

Water Sorption Characteristics of a New Type of Gelatine Powder, Produced by a New High-Pressure Micronisation Process

Christian Reibe and Željko Knez*

Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia

* Corresponding author: E-mail: zeljko.knez@uni-mb.si

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Abstract

A new high-pressure micronisation process for Gelatine has been developed. By applying this process to gelatine, a new type of Gelatine was produced: Dry and pure Gelatine powder of high molecular mass. This powder was investigated, regarding its sorption behaviour and compared to its feedstock material. The feedstock Gelatine was of type B 200 Bloom, 6 mesh, having a molecular mass of $150,000 \text{ g mol}^{-1}$. The produced Gelatine powder's molecular mass was around $130,000 \text{ g mol}^{-1}$, while its mean particle size was $300 \mu\text{m}$. Their sorption isotherms were investigated at $30 \text{ }^\circ\text{C}$, $40 \text{ }^\circ\text{C}$ and $60 \text{ }^\circ\text{C}$ and water activities in the range from 0.055 to 0.836. At given water activities the Equilibrium Moisture Contents (EMC) decreases with increasing temperature. The measured sorption isotherms were fit with the Brunauer-Emmett-Teller (BET)- model and the Guggenheim-Anderson-deBoer (GAB)- model. Both models described the adsorption behaviour well in their range of validity, while only the GAB-model was adequate for describing the desorption behaviour. Hysteresis effect occurred in each adsorption-desorption pair. The isosteric heat of sorption of both substances was determined for adsorption, desorption respectively. Slight differences in the sorption behaviour occurred due to processing, while quality of the gelatine was not affected.

Keywords: CO_2 -spray drying, Gelatine-powder; sorption isotherms; isosteric heat of sorption; Guggenheim-Anderson-deBoer -model; Brunauer-Emmett-Teller -model;

1. Introduction

The major challenge in the food industry is to guarantee a high product -safety, -quality and -stability,¹ while the water content is the most dominating factor in food systems². It strongly influences the physical and chemical properties and the systems' stability. To reach long term stability of food products by reducing the water concentration, drying processes like spray drying, freeze drying or convective drying, are commonly used. Spray drying is, due to economical advantages, one of the most favoured drying processes. But in certain cases, spray drying fails or requires a huge effort and different additives for atomising the wanted substance.

Due to its high molecular mass, Gelatine is one of those substances, being used as encapsulation material in a wide range of applications. It is extracted from collagen-containing resources (such as pigskin and cattle split) by thermal or enzymatic hydrolysis. It is not only used in the

pharmaceutical industry as encapsulation substance but also in food industry e.g. for the clarification of juice and beer and everywhere, where gelling agents, stabilisers, binding agents, emulsifying agents, foaming agents and thickening agents are needed. Furthermore, Gelatine is getting more and more important to "upgrade" common food products to functional food. Since Gelatine does neither comprise any fat nor carbohydrates nor cholesterol nor purine nor any preservatives it is a common, inoffensive additive to many applications.³

Different processes have been described, reporting the difficulties to atomise high molecular mass Gelatine. These days either completely hydrolysed Gelatine is spray dried or Gelatine, comprising a low molecular mass. To spray dry Gelatine of higher molecular mass, additives such as softeners or dusting agents- usually at least 4 times the amount of Gelatine - are used.⁴ Based on a high pressure technique, the PGSS-process,^{5,6,7} a new process was developed, that allows the micronisation and drying of high molecular mass Gelatine even from high concen-

trations in aqueous solutions. The result was a new type of Gelatine: Fine powderous, pure Gelatine of high molecular mass.⁸

Taking into account possible effects of the process on the Gelatine's nature such as hygroscopicity, adsorption and desorption effects, the sorption effects of this new Gelatine were investigated and compared to its granular feedstock Gelatine. Sorption isotherms show the points of hygroscopic equilibrium at defined water activities and at constant temperatures and pressures. The hygroscopic equilibrium is defined as the state where the moisture content of the substance is in equilibrium with its environment. It is depending on the temperature, the relative humidity and on the substances' nature. Sorption isotherms are essential for predicting and evaluating physical, chemical and microbiological stability, quality changes of foods during processing, as well as during storage.² In addition, they present essential parts of drying theories and provide necessary information for designing drying equipment and for studying the storage of dehydrated products.⁹ This study is focussed on the comparison of the sorption behaviour of a newly developed kind of Gelatine product- pure, micronised Gelatine powder, exhibiting a high molecular mass- and its feedstock granular Gelatine.

2. Experimental

2.1. Powder Production and Results

The investigated Gelatine powder was produced by applying the process,⁸ as presented in Figure 1. Supercritical carbon dioxide (scCO₂) was used as atomisation- and drying fluid, not only due to its advantageous critical point at moderate conditions, but also due to the relatively high solubility of water in this gaseous fluid. Feedstock Gelatine from type B, 200 Bloom, exhibiting a molecular mass of 150,000 g mol⁻¹ was used to prepare a 30 wt.-% aqueous Gelatine solution.

The solution then is stirred, heated and filled into a low-pressure vessel (1), which is stored on a balance (2) for measuring the gelatine flow. During the preparation of the starting solution, the spray tower (11) is preheated by flushing it with CO₂ that is delivered from a tank (6) and compressed by a pump (7) to supercritical conditions. A Coriolis-Flowmeter (8) determines the CO₂-flow that is downstream preheated by a coil heat exchanger (9). The flow can be controlled by a valve (5). The heated scCO₂ then is expanded through a nozzle (10) into the isolated spray tower (11) for heating it up. As soon as the required temperature in the spray tower remains constant, the experiment can be started.

For starting the experiment, the gelatine sol is delivered by a pump (3) and introduced to the flowing scCO₂ by opening a valve (4). Due to tubular flow in the tube, the two substances, gelatine sol and CO₂ are mixed. The mixture then is expanded through the nozzle (10). Due to the

rapid expansion of the CO₂, in contrary to a relatively poor expansion of the gelatine sol, the mixture was divided into finest particles into the spray tower.

Proper parameters were found to suppress the cooling effect, due to the CO₂'s Joule Thomson effect, to support the removal of water by evaporation and to obtain optimum solubility of water in CO₂. The exhaust gas-water flow passes a cyclone (12), to separate the fine fraction from the gas and stores it in an extra vessel (13). The exhaust gas is withdrawn by a vent (14).

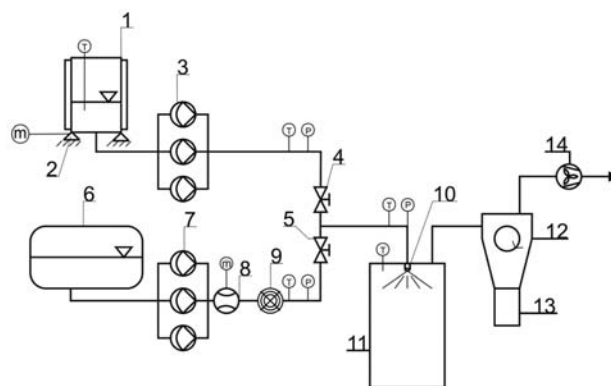


Figure 1: Process scheme

Leading parameters for successful spray dry experiments were the pre-expansion temperature and pre-expansion pressure as well as the ratio CO₂/Gelatine-solution and the spray tower temperature. Continuous experiments, resulting in a dry gelatine powder were gained, when the pre-expansion pressure was slightly above the supercritical point of CO₂, while the post-expansion temperature was at around 60 °C. CO₂-Gelatine ratios around 15 were found to be sufficient for a successful drying. The resulting dry gelatine powder has a mean particle size of approximately 300 μm, while its molecular mass was around 130,000 g mol⁻¹.

2.2. Determination of the Sorption Isotherms

The determination of the moisture sorption isotherms in this work was performed, according to the standard isopiestic (also known as salt-; or static-gravimetric) method.^{10,11,12} This method is measuring a substance's water uptake (or water loss), when it is exposed to an atmosphere of a defined relative humidity. The relative humidity is set in a closed system by preparing saturated solutions from deionised water and a chosen salt at constant temperatures. The samples are exposed to this atmosphere to absorb water until the hygroscopic equilibrium is achieved.¹⁰

Five salts were chosen to set relative humidity between 0.074 and 0.836 at 30 °C, between 0.063 and 0.823

Table 1: Equilibrium relative humidity above saturated salt solutions at different temperatures (according to Greenspan¹⁴ and Maroulis¹⁵)

T [°C]	Equilibrium relative humidities					
	KOH	LiCl	MgCl ₂	Mg(NO ₃) ₂	NaCl	KCl
30	0.074 ± 0.006	0.113 ± 0.002	0.324 ± 0.001	0.514 ± 0.002	0.751 ± 0.001	0.836 ± 0.003
40	0.063 ± 0.004	0.112 ± 0.002	0.316 ± 0.001	0.484 ± 0.004	0.746 ± 0.001	0.823 ± 0.003
60	0.055 ± 0.003	0.11 ± 0.003	0.293 ± 0.002	0.44 ¹⁵	0.745 ± 0.003	0.803 ± 0.004

at 40 °C and between 0.055 and 0.803 at 60 °C. The data was determined from Greenspan¹⁴ except the value for Magnesium Nitrate at 60 °C, which was taken from Maroulis et al.¹⁵. Table 1 shows the values for the equilibrium relative humidity for saturated salt solutions, at the three chosen temperatures (30 °C, 40 °C, 60 °C), prepared with the six chosen salts.

The saturated salt solutions were prepared in desiccators. To ensure saturation, an excess of crystalline salt was always present at the bottom of the desiccators. For maintaining the equilibrated, temperature-dependending relative humidity, the desiccators were placed in the tempered oven two days prior to the start of the sorption experiments.

2. 2. 1. Adsorption

Masses of 0.5 g (± 0.01 g) of the Gelatine powder and 4 g (± 0.2 g) of the feedstock Gelatine granulate were weighed into glass jars on a laboratory scale (Kern 770–14). According to the standard for the determination of water and ash contents in edible Gelatine¹⁶, the samples were dried at 105 °C (± 2 °C) for 48 hours. After they were cooled down to room temperature in a dry atmosphere, the samples were weighed again and placed in the desiccators, containing the saturated salt solutions. In certain intervals their mass was determined gravimetrically. To reduce the effects of atmospheric adsorption or desorption, the total time for the weighing procedure was minimised.² After the hygroscopic equilibrium was achieved, the samples were dried again, according to the standard method.

2. 2. 2. Desorption

For the desorption experiments, samples were equilibrated in atmospheres, exhibiting the same relative humidities like those, used for measuring the adsorption experiments. Starting with Sodium Chloride, the samples were equilibrated first at higher relative humidity. Then they were placed stepwise in desiccators, containing lower relative humidity until the hygroscopic equilibrium at the lowest relative humidity, obtained by Potassium Chloride, was achieved.

The EMC “ X_e ” is determined by relating the increase in weight ($m_2 - m_1$) to the weight of the dry sample (m_1):

$$X_e = \frac{m_2 - m_1}{m_1} \quad (1)$$

Due to the fast water uptake in the initial stages of sorption experiments of Gelatine, the starting measurements were done after 1, 3, 5 and 10 hours. Then the weight was measured every 24 hours until the samples' weight did not change in two consecutive measurements for more than 0.002 g. The hygroscopic equilibrium was reached. The dry basis was also determined according to the standard for the determination of water and ash contents in edible Gelatine.

2. 3. Modelling of the Ad- and Desorption Isotherms

According to McLaughlin and Magee,¹⁷ water activity is defined as the vapour pressure of water in food (p_f) to the vapour pressure of pure water (p_0) at the same temperature and therefore an expression of the equilibrium relative humidity (e.r.H.):

$$a_w = \frac{p_f}{p_0} = \frac{e.r.H.}{100} \quad (2)$$

The International Union of pure and applied chemistry (IUPAC) recommends, in a report of the commission on colloids and surface chemistry, the so called Brunauer-Emmet-Teller (BET) plot as standard evaluation for monolayer values in the water-activity range from 0.05 to 0.3.¹⁸ It can be derived from kinetic and statistical mechanics as well as from thermodynamic approaches.¹³

This model is described by the following equation:

$$X_e = \frac{c_1 \cdot c_2 \cdot a_w}{(1 - a_w)[1 + (c_2 - 1)a_w]} \quad (3)$$

in the linearised form:

$$\frac{a_w}{(1 - a_w)X_e} = \frac{1}{c_1 \cdot c_2} + \frac{c_2 - 1}{c_1 \cdot c_2} a_w \quad (4)$$

“ X_e ” describes the equilibrium moisture, a_w the water activity. “ c_1 ” is the BET-monolayer moisture content according to the dry basis, while “ c_2 ” is a constant, related to the net isosteric heat of sorption.¹³

The Guggenheim-Anderson-deBoer (GAB) model is an improvement of the Langmuir and BET-model by adding an additional factor “ X_m ”.¹⁹

$$\frac{X_e}{X_m} = \frac{c_3 \cdot c_4 \cdot a_w}{(1 - c_4 \cdot a_w)(1 - c_4 a_w + c_3 \cdot c_4 \cdot a_w)} \quad (5)$$

linearised in the following form:

$$\frac{a_w}{X_e} = \frac{1}{X_m \cdot c_3 \cdot c_4} + \frac{\left(1 - \frac{2}{c_3}\right)}{X_m} a_w + \frac{c_4}{X_m} \left(\frac{1}{c_3} - 1\right) a_w^2 \quad (6)$$

“ X_m ” is the GAB monolayer moisture content related to the dry basis. It is a measure for the material’s availability of active sites for water sorption.¹⁹ “ c_3 ” is a constant, related to the monolayer heat of sorption. It is a measure of the strength of binding water to the primary binding sites. The larger its value, the stronger is the water bound in the monolayer.¹⁹ “ c_4 ” is a factor related to the heat of sorption of the multilayer.¹³ The more the adsorbed molecules are structured in a multilayer, the lower is the value of “ c_4 ”.¹⁹

The most widely accepted and representative model for sorption isotherms for food has been the Guggenheim-Anderson-deBoer (GAB) -model.²⁰ This is mainly due to its accuracy and its validity over a wide range of water activities from 0.1 to 0.9.

The BET-model constants (c_1, c_2) can be determined by plotting the quantity ($a_w / ((1 - a_w) X_e)$) versus the water activity at a fixed temperature.²¹ The resulting function in the form $Y = ax + b$ provides the values for the calculation of the BET-Parameters according to the following substitutions to Equation 2:

$$Y = \frac{a_w}{(1 - a_w) X_e}; \quad a \cdot x = \frac{(c_2 - 1)}{c_1 \cdot c_2}; \quad b = \frac{1}{c_1 \cdot c_2}$$

The determination of the GAB-model constants is done similar. Due to the polynomial character of the linearised GAB-Equation (Equation 5), a polynomial fitting provides the terms for calculating the GAB model constants.²¹ Therefore the quantity of a_w / X_e at a fixed temperature is plotted versus the water activity.

The resulting function in the form $Y = a + bx + cx^2$ provides the values (a, b, c) for the following terms of the linearised GAB-equation (Equation 4):

$$Y = \frac{a_w}{X_e}; \quad a = \frac{1}{X_m \cdot c_3 \cdot c_4};$$

$$bx = + \frac{\left(1 - \frac{2}{c_3}\right)}{X_m} a_w; \quad cx^2 = \frac{c_4}{X_m} \left(\frac{1}{c_3} - 1\right) a_w^2$$

Quality of the fits was calculated with the relative percentage deviation modulus, according to equation 6:

$$\%E = \frac{100}{n} \cdot \sum \left(\frac{|m_i - m_i'}{m_i} \right) \quad (7)$$

While n is the number of measured points, m_i are the measured values and m_i' are the values, predicted by the

GAB- model. Generally, it is assumed that a good fit was done, when %E is less than 10 %^{17,22}.

2. 4. Determination of the Net Isosteric Heat of Sorption

The net isosteric heat of sorption (q_{st}) is an important thermodynamic parameter, which measures the binding energy of the forces between the water vapour molecules and the solid.²³ It is defined as the difference between the amount of energy, which is required to remove water from a material (Q_{st}) and the amount of energy, which is required for water vaporisation (ΔH_v):

$$q_{st} = Q_{st} - \Delta H_v \quad (8)$$

The isosteric heat of sorption can be derived from sorption isotherms at several temperatures using the following Equation 8, which is derived from the Clausius-Clapeyron Equation:

$$\frac{\partial \ln(a_w)}{\partial T} = \frac{q_{st}}{RT^2} \quad (9)$$

Assuming that the isosteric heat of sorption is invariant with temperature, the following expression is found:

$$\ln(a_w) = - \left(\frac{q_{st}}{R} \right) \cdot \frac{1}{T} + c \quad (10)$$

The net isosteric heat of sorption can be calculated by plotting the sorption isotherm as $\ln(a_w)$ versus $(1/T)$ for certain values of the material moisture content and then determining the slope which is equal to q_{st}/R .²³

This method has to be questioned in the case of significant hysteresis effects.²² Hysteresis is a signal for thermodynamically irreversible phenomena. Iglesias et al. concluded that the heats of changes due to the changes in sorption are negligible, compared to the overall energy changes.²⁴ Therefore, this method for the determination of the isosteric heat of sorption allows a qualitative description of the sorption process.

3. Results and Discussion

3. 1. GAB- and BET- Model Fittings

The experimental data of the starting Gelatine material (so-called feedstock Gelatine or original) was fitted with the GAB- model and the BET- model. In Figure 2 it is exemplified at the 40 °C-isotherm that the adsorption-, as well as the desorption-curves are well described by the GAB- model. The standard deviation is indicated by the error bars. As can be seen from Figure 2, only at high water activities around 0.8 small deviations of 0.85% occurred within six reproducibility experiments.

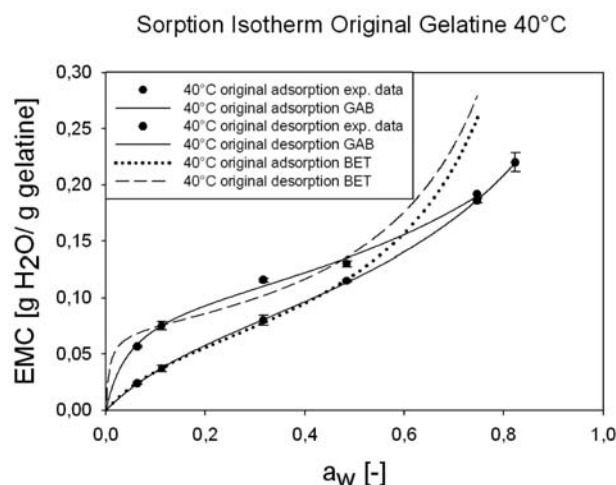


Figure 2: Adsorption- and desorption- isotherms of original Gelatine at 40 °C fitted with the BET and the GAB model

The BET- model describes the adsorption well in its recommended range of validity ($a_w = 0.05\text{--}0.3$) and even slightly above to approx. $a_w = 0.5$. The estimated parameter values for the adsorption- and the desorption-isotherms for the original, feedstock Gelatine granulate and the Gelatine powder are presented in Table 2. The monolayer moisture content was in the range from 6.26 % to 12.99 %. But the monolayer moisture content of the powder Gelatine was always less compared to its feedstock Gelatine.

adsorption parameter. The deviation modulus for the desorption isotherms presents less acceptable fittings, while it improves with increasing temperature.

3. 2. Sorption Isotherms

Figure 3 presents the sorption isotherms of the feedstock Gelatine and the produced Gelatine powder at 30 °C, 40 °C and 60 °C.

The isotherms for adsorption as well as for desorption are of sigmoid shape which classifies them as Type II isotherms. This Type of isotherm is typical for material from biological origin²⁴ and already indicates localised sorption, which reasons the applicability of the GAB-model². An increase of the water activity at constant temperature results in higher EMC's, while a temperature increase at constant water activity results in lower EMC's. The higher EMC's at higher water activities are due to an inability of the substance to maintain vapour pressure in unity with decreasing moisture content. With decreasing moisture content, the moisture in the food tends to show a lower vapour pressure, acting as if in solution, changing with atmospheric humidity.¹⁷ It is these changes in vapour pressure in the food with atmospheric humidity, which result in the characteristic sigmoid shape of water sorption isotherms.²⁵ The decrease of the EMC's with increasing temperature may be explained by the excitation states of molecules. The excitation state of molecules is increasing with increasing temperature. Thus, their distances apart

Table 2: Parameter values and deviation modulus of the GAB-model and the BET- model for the investigated Types of Gelatine

	Adsorption feedstock Gelatine			Desorption feedstock Gelatine			Adsorption powder Gelatine			Desorption powder Gelatine		
	30 °C	40 °C	60 °C	30 °C	40 °C	60 °C	30 °C	40 °C	60 °C	30 °C	40 °C	60 °C
GAB												
X_m	0.085	0.091	0.058	0.112	0.097	0.067	0.08	0.083	0.057	0.103	0.089	0.072
c_3	8.178	6.575	8.822	25.72	31.08	12.47	9.298	7.301	5.959	22.27	25.43	6.932
c_4	0.798	0.753	0.962	0.587	0.677	0.856	0.819	0.783	0.938	0.621	0.680	0.841
%E	1.45	0.97	0.12	2.7	3.02	1.2	2.94	4.1	3.15	3.68	4.01	1.46
BET												
c_1	0.068	0.069	0.056	0.073	0.071	0.057	0.065	0.064	0.053	0.068	0.065	0.06
c_2	9.468	7.472	9.015	170.4	141.2	15.29	10.83	8.648	6.226	104.7	73.57	7.719
%E	0.5	1.69	1.91	10	9.97	8.76	3.38	7.56	3.12	11.23	10.87	4.49

The monolayer moisture content of Gelatine is depending on its molecular mass. The lower the molecular mass, the lower is the monolayer moisture content.¹³ That means, although the molecular mass was decreased only for around 20,000 g mol⁻¹, it already had a visible effect on water adsorption.

The estimated deviation modulus shows the accuracy for both substances at each isotherm. The deviation modulus for the GAB-model shows a high accuracy, due to the low values of % E (0.12 to 4.1 < 10). The high accuracy is also obvious from Table 1. In the case of the BET model, acceptable values for % E are only given for the

are extended and their attractive forces reduced. This leads to a lessened water sorption with increasing temperature at constant water activities.¹⁷

In the case of the 40 °C and the 60 °C-isotherm, the EMC's are converging with the ones at lower temperatures for water activities above 0.44 for both types of Gelatine in ad- and desorption. The effects of a high equilibrium relative humidity and a high temperature led to a sol-forming of the substances. Therefore the sorption behaviour was remarkably changed. But, contrary to the original Gelatine, the powder's EMC did not converge for the case of the 30 °C and the 40 °C isotherm. Obviously

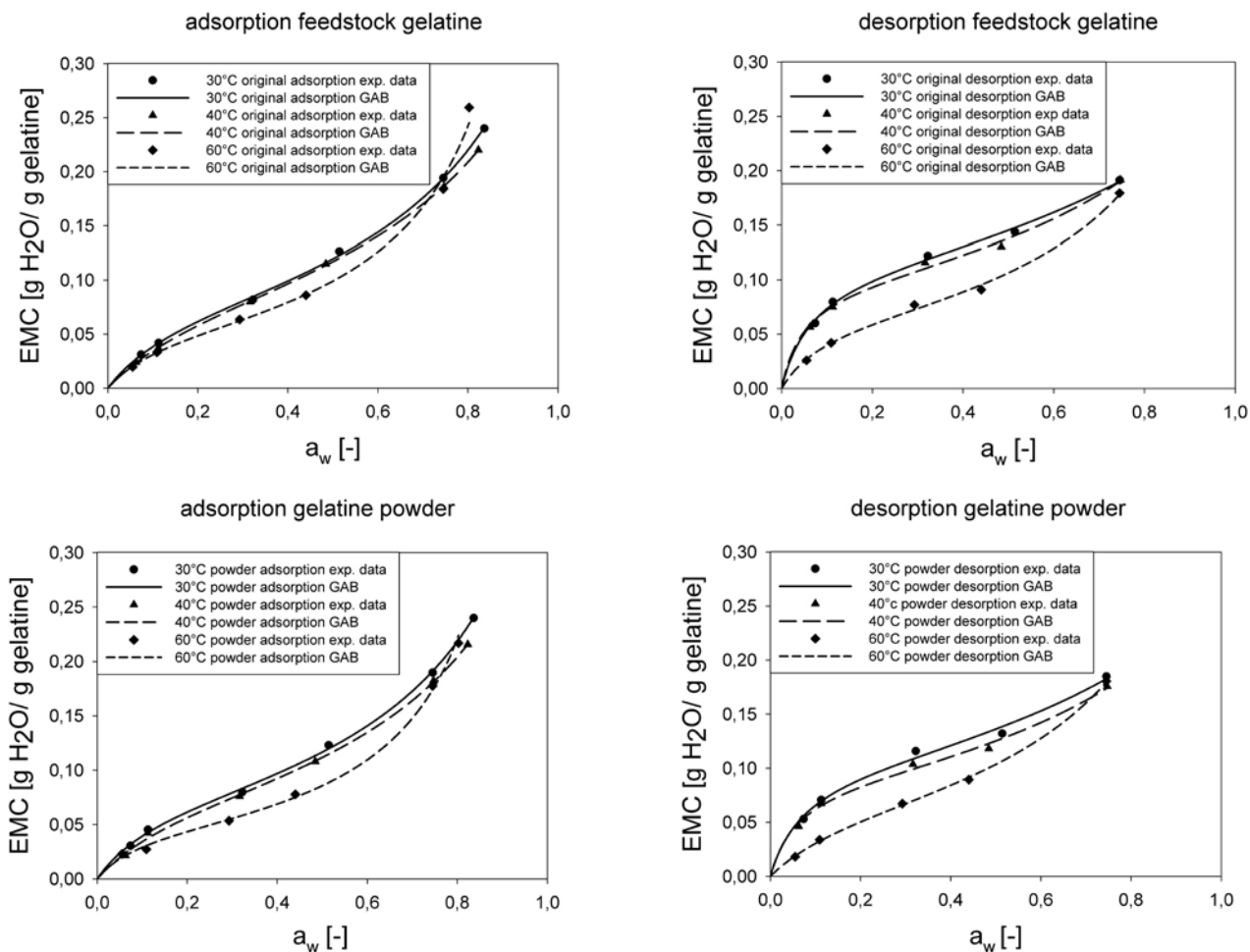


Figure 3: Adsorption and desorption isotherms of the feedstock Gelatine and the Gelatine powder at 30 °C, 40 °C, 60 °C- experimental data fitted with the GAB- model

the Gelatine powder is less affective to the temperature and the high relative humidity.

In each case hysteresis occurs, while the differences are getting less with increasing temperature. Hysteresis means the difference between adsorption and desorption at constant water activity and constant temperature. Common explanations for hysteresis to occur are thermodynamically irreversible processes. Despite this assumption the phenomenon is not yet well understood.²⁶ One theory to explain hysteresis is, that in the wet conditions the polar sites onto which water is sorbed, are not entirely satisfied.¹⁷ During the drying process, the water holding sites are drawn close enough together with shrinkage to satisfy each other. This results in less water binding capacity during adsorption.

Figure 4 exemplifies the differences in sorption behaviour between the Gelatine granulate and the Gelatine powder at the 40 °C-isotherm.

It is shown, that there exist slight differences in the EMC's for adsorption and desorption at given water activities and given temperature. The EMC's of the Ge-

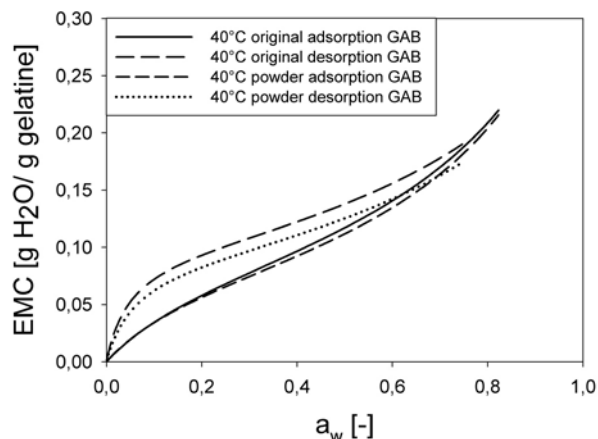


Figure 4: Example for the differences feedstock (original) Gelatine to Gelatine powder

latine powder are slightly lower than those of the Gelatine granulate although the change in molecular mass was relatively small. Nevertheless, this little change in

molecular mass is sufficient to result in less water binding capacity and the deviations between both formulations.

3. 3. Kinetic Observations

The most significant difference between the feedstock Gelatine and the Gelatine powder is the time that is required to equilibrate the samples, although the values of the EMC's remain almost the same. Figure 5 exemplifies qualitatively this difference in the case of the time which is required to equilibrate the feedstock Gelatine, respectively the Gelatine powder, in an atmosphere of 0.322 water activity at 30 °C, in an atmosphere of 0.316 water activity at 40 °C and in an atmosphere of 0.293 at 60 °C.

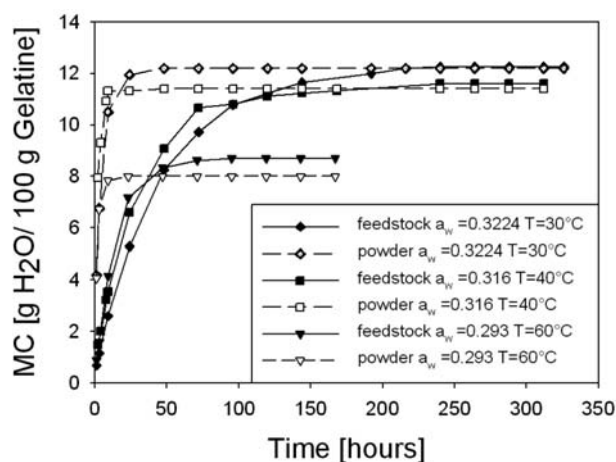


Figure 5: Time for equilibrating feedstock Gelatine and Gelatine Powder at $a_w = 0.3224$ ($T = 30\text{ °C}$) $a_w = 0.316$ (40 °C) and $a_w = 0.293$ (60 °C)

It is shown that the Gelatine powder is equilibrated at 30 °C after approximately 40 hours, while the feedstock Gelatine required approx. 260 hours. At 40 °C the Gelatine Powder is equilibrated after approx. 20 hours, while the feedstock Gelatine requires approx. 240 hours. The Gelatine powder at 60 °C is also equilibrated at around 20 hours, while the feedstock Gelatine required approximately 100 hours. It should be noted, that the EMC of the feedstock Gelatine is slightly higher than the powders EMC. This effect gets a little stronger the higher the temperature is. The most obvious reason for this observation is the enlarged surfaces of the Gelatine powder compared to the feedstock granulate. Thus, the surface of the water binding sites and therefore the water binding capacity is increased.

3. 4. Isotheric Heat of Sorption

In Figure 6, the net isotheric heat of ad- and desorption for the feedstock Gelatine and Gelatine powder are

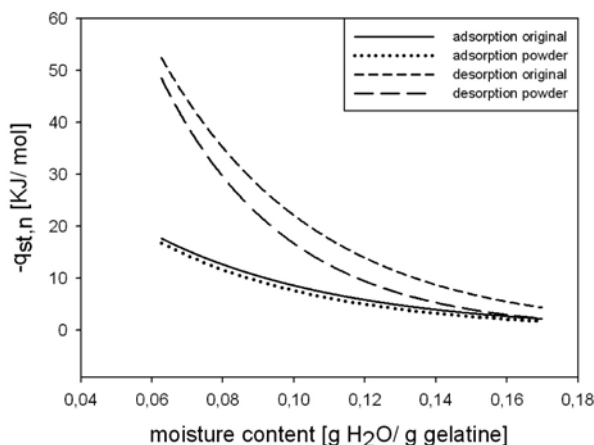


Figure 6: Net isotheric heat of adsorption and desorption of the feedstock Gelatine and the Gelatine powder for different moisture contents and the temperature range from 30 °C to 60 °C

plotted versus moisture content for the temperature range from 30 °C to 60 °C.

The bases for these determinations are the calculated GAB values. It is clearly shown, that the net isotheric heat of sorption is increasing (getting less negative) with increasing moisture content. The increase at low moisture contents is due to the availability of active polar sites of the material at the initial stages of sorption that are covered with water, forming a monomolecular layer.²⁷ Furthermore, the net isotheric heat of sorption for the desorption is lower (more negative) than for adsorption, until it converges at moisture contents above 0.16. As explanation for this effect, Benado et al.²⁸ suggested that there are more active polar sites on the material during desorption and thus the binding is stronger. The steep increase at low moisture contents is due to the availability of highly active polar sites of the material at the initial stages of sorption that are covered with water, forming a monomolecular layer.²⁷ Figure 6 clearly shows that the Gelatine powder's values for the isotheric heat of sorption are lower than the granular Gelatines' one. This shows less sensitivity of the Gelatine powder to temperature changes. It also indicates that the binding is lower, which is a result from a higher heat and mass transfer, due to the enlarged surface of the powder.

4. Conclusion

The sorption behaviour of a new type of spray dried Gelatine powder was investigated and compared to its starting material: Type B Gelatine having a molecular mass of $150.000\text{ g mol}^{-1}$. The newly developed spray drying process for Gelatine is capable to atomise and dry high molecular mass Gelatine from high concentrated aqueous solutions. The resulting powder was a pure and

dry Gelatine powder exhibiting a high molecular mass of around 130,000 g mol⁻¹. The adsorption and the desorption isotherm of the two substances were determined at 30 °C, 40 °C and 60 °C and fit with the Brunauer Emmet Teller (BET) and the Guggenheim Anderson deBoer (GAB) –model. It was found that the sorption isotherms of both types of Gelatine exhibit a sigmoid shape. Temperature affects the sorption isotherms: At constant water activity, lower values for the EMC were found at higher temperatures. Each isotherm shows hysteresis, meaning higher values for the EMC for desorption compared to adsorption at constant water activities and constant temperatures. The values for the EMC for adsorption as well as for desorption are higher at higher water activity and constant temperature. Although the decrease in molecular mass was relatively small (around 20,000 g mol⁻¹), the EMC's for the spray dried Gelatine powder were always less in the case of the Gelatine powder, compared to the Gelatine granulate. Furthermore, the sorption isotherms of the Gelatine powder at 30 °C, 40 °C and 60 °C do not tend to converge at higher water activities. It seems as if the gel forming is slightly provided in the case of the fine powderous Gelatine. Both regression models describe the adsorption behaviour well in their recommended range of validity, while the BET- model fails to describe sorption behaviour at water activities above its recommended rang. It also shows deviation modules out of the range for acceptable fittings in the case of desorption. Gelatine powder is 5 to 12 times faster in reaching the EMC compared to the Gelatine granulate, depending on the temperature. Higher temperature leads to a faster achievement of the EMC. The net isosteric heat was observed to increase with a decrease in moisture content, and decrease with increasing temperature. It is also higher for desorption than adsorption at low moisture contents, indicating that desorption requires more energy than adsorption. Less energy was required for adsorption and desorption of the Gelatine powder, which was found to be an effect of the enlarged powder's surface. These observations not only play an important role for the design of preservative drying process designs, they also show that the Gelatine's sorption characteristics have not been affected by the high-pressure, supercritical CO₂ atmosphere during the new spray dry process.

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Notation

a_w	water activity	[-]*
c	constant	[-]
c_1, c_2	BET model constants	[-]
c_3, c_4	GAB model constants	[-]
ΔH_v	energy, needed for water vapourisation	[J mol ⁻¹]
e.r.H.	equilibrium relative humidity	[%]
m_1	mass of the dry sample	[kg]
m_2	mass of moisture loaded sample	[kg]
%E	deviation modulus	[%]
MC	moisture content	[%]
m_i	measured values	[kg]
m_i'	values predicted by the GAB model	[kg]
n	number of measured points	[-]
Q_{st}	total heat of sorption	[J mol ⁻¹]
q_{st}	net isosteric heat of sorption	[J mol ⁻¹]
R	universal gas constant	[KJ (mol K) ⁻¹]
T	temperature	[K]
X_e	EMC (equilibrium moisture content)	[%]
X_m	GAB monolayer moisture content	[%]

* [-] = dimensionless

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Povzetek

Razvili smo nov visokotlačni postopek za mikronizacijo želatine. S tem postopkom dobimo nov tip čiste želatine visoke molske mase v prahu. Lastnosti dobljenega produkta smo primerjali z izhodnim materialom, ki je bil tipa B 200 Bloom, 6 mesh, z molsko maso $150,000 \text{ g mol}^{-1}$. Dobljeni produkt je imel nekoliko nižjo molsko maso, okoli $130,000 \text{ g mol}^{-1}$, medtem, ko je bila srednja velikost zrn dobljenega produkta $300 \mu\text{m}$. Sorpcijske lastnosti dobljenega produkta smo študirali pri temperaturah $30 \text{ }^\circ\text{C}$, $40 \text{ }^\circ\text{C}$ in $60 \text{ }^\circ\text{C}$ in pri vlažnostih med 0.055 to 0.836. Pri danih vlažnostih je bila določena ravnotežna vlažnost materiala, ki se znižuje z povišano temperaturo. Izmerjene sorpcijske izoterme so bile modelirane z Brunauer- Emmet- Teller (BET)- modelom in Guggenheim- Anderson- deBoer (GAB)- modelom. Oba modela dobro opišeta adsorpcijske lastnosti v območju njihove veljavnosti, medtem ko je bil GAB-model ustrežnejši za opis desorpcijskih lastnosti. Histerezo smo opazili pri vseh adsorpcijsko – desorpcijskih parih. Določene so bile sorpcijske toplote. Med procesom mikronizacije se sorpcijske lastnosti želatine spremenijo le malenkostno, medtem ko proces mikronizacije nima večjega vpliva na kvaliteto želatine.