

**COMPARING THE SORPTIVE PROPERTIES OF SELECTED BRANDS OF INSTANT COFFEE
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Key words: instant coffee, lyophilization, sorption isotherms, monolayer capacity, specific surface of sorption, water activity, energy constant, BET

Sorption isotherms of the tested brands of instant coffee were determined by the static desiccator method at 20°C. The equilibrium water content was significantly ($\alpha=0.05$) dependent on the product type and water activity (a_w). A distinct increase in water content was observed in the coffees K2 and K3 at the value of a_w about 0.70 and in coffee K1 at the value of a_w about 0.50. Above specified value of a_w it is likely that capillary condensation occurred. The monomolecular layer capacity was determined from the BET equation (K1 – 6.3044; K2 – 5.0424; K3 – 6.7225 g/100 g of the dry substance); this, in turn, was used to calculate the specific surface of sorption (K1 – 221; K2 – 177; K3 – 236 m²/g). The value of a_w corresponding to water content at the monolayer level was also determined, thereby estimating the storage durability of particular coffee brands. The value of the energy constant, calculated from the BET equation (about 20 kJ/mol) indicated that the process of adsorption in the experiment was a physical phenomenon.

INTRODUCTION

The growing interest in the sorptive properties of instant coffee is caused by increasing demand for convenient food.

The quality of instant coffee is determined primarily by its taste, flavour and colour. However, it is also important to a consumer how easily and quickly a product can be restored (prepared for consumption by hydration) and how durable it is in storage. These parameters are used to characterise convenient food [Ratti, 2001].

An especially important parameter affecting the culinary properties of instant coffees are their sorptive properties, closely linked to their restorability and durability in storage. The parameter depends on the structure and composition of coffee particles.

The study explores the differences in sorptive properties between three brands of instant coffee, commercially available in Poland, based on the sorption isotherms and the parameters calculated from them.

MATERIALS AND METHODS**Materials**

Three brands of instant coffee from different manufacturers and from various price ranges were used as the research material. Two of them were obtained by spray-drying of coffee extracts (K2 – medium price, K3 – low price), whereas the third one was obtained by lyophilization (K1 – high price). All the samples were taken from coffee purchased at one of the supermarkets in Gdynia.

The shape of the lyophilised coffee particles of the coffee brand K1 was briquette-like, with a compact structure and

light colour. Coffee brand K2 was obtained by spray-drying, its particles had a form of granules (formed in the process of agglomeration) with a compact structure and darker colour than coffee brand K1. The coffee brand K3 was spray-dried, its particles were also granular (agglomeration), with an open structure and a dark brown colour.

The coffees were packed in glass jars with twist-off caps.

Considering the effect of the technological process (conventional drying and lyophilization) on the agglomerates physical properties, the following are the results of determination of granulometric distribution of the tested coffee samples (Table 1).

All the reagents used for preparing the saturated salt solutions were of the pure analytical grade.

Methods

The sorption isotherms were measured by the static desiccator method, using saturated salt solutions (Table 2).

The static desiccator method consists of the determination of the humidity equilibrium between the analysed sample and the atmosphere of an established relative humidity, adjusted with saturated salt solutions. Based on the measurement of the change in the weight of a product sample, placed

TABLE 1. Granulometric distribution of the tested coffee brands (f (mm)).

Coffee	f>2.5	2.0<f<2.5	0.8<f<2.0	0.2<f<0.8	f<0.2
K1	10.8	24.9	59.5	4.3	0.5
K2	28.7	26.8	35.6	4.1	4.8
K3	18.3	10.8	39.3	21.7	9.9

TABLE 2. Water activity of saturated salt solutions.

Salt	Water activity (20°C)
NaOH	0.0698
LiCl	0.1114
CH ₃ COOK	0.2310
MgCl ₂	0.3303
K ₂ CO ₃	0.4400
Na ₂ Cr ₂ O ₇	0.5480
KJ	0.6986
NaCl	0.7542
KCl	0.8513
KNO ₃	0.9320
K ₂ Cr ₂ O ₇	0.9793

over a salt solution of known water activity, the water content in the product is determined. The scope of research included the water activity (a_w) range from 0.07 do 0.98. The experiment was conducted at the temperature of 20°C. The equilibrium was established after 90 days [Tyszkiewicz, 1987; Świtka, 1992; Krelowska-Kułas, 1993].

For the evaluation of the results, BET adsorption isotherm was applied. In order to determine the parameters of the sorption process, such as the monomolecular layer capacity together with the corresponding water activity and energy constant, the following form of the BET equation was applied:

$$v = \frac{v_m c a_w}{(1 - a_w)[1 + (c - 1)a_w]} \quad (1)$$

where: v – adsorption (g/g); v_m – maximum adsorption value corresponding to the whole area covered by a monomolecular layer of the adsorbate (g/g); c – a constant which is linked exponentially with the difference between the heat of adsorption on the first and consecutive layers, assumed to be constant and equal to the heat of condensation (kJ/mol); a_w – water activity (-), [Ościk, 1979; Paderewski, 1999; Atkins, 2003].

The classical BET multilayer sorption equation is still used to calculate monolayer values in very different physico-chemical fields, and it has the approval of the International Union of Pure and Applied Chemistry (IUPAC) [Timmermann, 2003].

Parameters of the above equation were identified from empirical data. Identification was conducted by means of non-linear regression using a non-gradient algorithm. Such an approach avoids stopping the estimation process by a local minimum. Minimization of the sum of square residuals was adopted as the function of lost. This criterion is the most extensively applied in the statistical analysis.

Knowing the value of water adsorbed at the temperature below the boiling point and the so-called “water cross-section”, the adsorbent specific surface was calculated from the following equation:

$$a_{sp} = \omega \frac{v_m}{M} N \quad (2)$$

where: a_{sp} – specific surface of sorption (m²/g); N – Avogadro number (6.023×10^{23} molecules/mol); M – molecular weight of water (18 g/mol); ω – water cross-section (1.05×10^{-19} m²/molecule) [Ościk, 1979; Paderewski, 1999; Atkins, 2003].

RESULTS AND DISCUSSION

Food is usually dried by conventional methods (hot air), which employ the action of elevated temperature (35-95°C) at the atmospheric pressure. Drying is then the effect of evaporating water from a product's surface. Among the major benefits of the conventional drying is its low cost [Nijhuis *et al.*, 1996]. However, more sensitive products, either liquid or solid (*e.g.* coffee, juices, strawberries, mushrooms) are now usually dried by lyophilization [Ratti, 1994; Irzyniec *et al.*, 1995]. The process consists in sublimation from the interface, which results in preserving the natural taste, flavour and colour of the substance [Krokida *et al.*, 1998; Lin & Durance, 1998]. It must be stressed, however, that the cost of lyophilization is about five times greater than that of conventional drying [Lorentzen, 1979; Ratti, 2001].

Important parameter differences of the quality lyophilized and conventionally dried food (especially coffee) is its susceptibility to rehydration. Products dried by conventional methods rehydrate slowly and not always completely, unlike lyophilizates, whose rehydration is quick and almost complete. Very good rehydration, which is a measure of damage of the structure of components and protein denaturation, is also an indication of a low degree of changes of proteins and carbohydrates in the lyophilization process [Ratti, 1994].

The comparison of the sorptive properties was based on the evaluation of:

- mutual position of adsorption isotherms, determined at 20°C [Makać & Urbanek-Krzysztofiak, 2000],
- the parameters of adsorption isotherms, based on the BET model [Ościk, 1979; Tyszkiewicz, 1987; Świtka, 1992; Paderewski, 1999; Atkins, 2003].

The relationship between the equilibrium water content in a product and its water activity is presented in a graphic form (Figure 1) as isotherms of sorption. For all the coffee brands tested in the experiment, the isotherms had a sigmoidal shape, described in the literature as type II in Brunauer's classification. Thus determined isotherms reflected the adsorption process taking place on porous materials. A sigmoid-

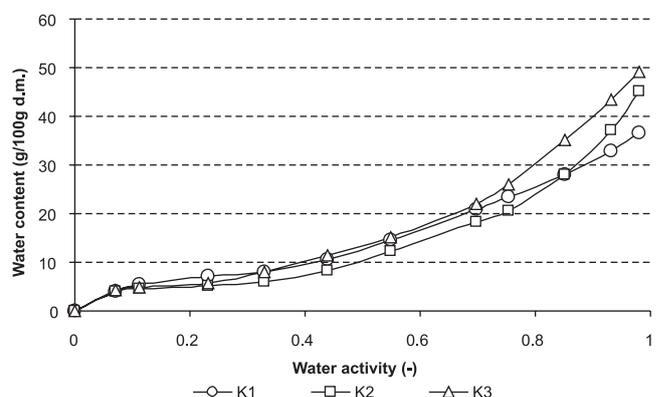


FIGURE 1. Sorption isotherms of selected coffee brands, determined at 20°C.

dal shape of the sorption curves indicated that multimolecular layers of water were created on the surface of coffee particles [Ościk, 1979; Świtka, 1992; Paderewski, 1999].

Water adsorption by the tested coffees grew together with a_w . The coffee K3 was characterised by a higher sorptive capacity than the other coffees (K1, K2) in almost the whole range of water activity. Considering the fact that instant coffees are waterless extracts of natural coffee, which makes them similar in terms of their chemical composition, the differences in the coffees sorptive capacity should be caused by the varied micro- and macroscopic structures of their particles (Table 1). The structure of coffee particles is a result of the denaturing effect of high temperature on protein and carbohydrate fractions during the drying process and the application of a particular agglomeration method in the technological operations. It is probably the porosity (macrostructure) of the coffee K3 particles, shaped during the particle agglomeration, that made water diffusion easier, thereby increasing the sorption value.

After exceeded limit $a_w = 0.70$ the absorption effect became particularly visible. It is possible that capillary condensation takes place over $0.70 a_w$ in the coffees tested in the experiment.

When the goodness-of-fit test for multiple populations was performed, it was shown that a zero hypothesis to the effect that there are no differences in the sorptive capacity of the coffee brands should be rejected. The critical value of χ^2_α for 10 degrees of freedom and the significance level $\alpha=0.05$ was 18.307 and was lower than the calculated value of $\chi^2 = 98.941$. Therefore, the coffee brands tested in the experiment were different in terms of their sorptive capacity.

The course of sorption isotherms within the interval from 0.07 - $0.54 a_w$ range enabled determining the BET equation, by assaying the goodness of its fit (root mean square error, Pearson's linear correlation coefficient) to empirical data, as well as calculating parameters (v_m , c , a_w) of the BET equation. The results obtained are presented in Table 3.

The values of the linear correlation coefficient (r) indicate that estimated isotherm model in 96-99% was convergent with empirical data. While the values of root mean square error indicate that parameters of BET equation estimated with error within the range 0.53 - 1.85 .

The monolayer capacity (v_m), determined from the BET equation, describes the sorption capacity of adsorbents, and, consequently, the availability of polar sites for water molecules. Using the notion of a monolayer, various aspects of physical and chemical decaying of dry products and their susceptibility to hydration can be analysed [Lorentzen, 1979; Mathlouthi, 2001].

The highest monolayer capacity was found in the coffee K3, while the lowest was in K2. Both coffees (K2 and K3) were obtained by spray-drying, but the structure of their parti-

cles was different. In the coffee K3 the dominant fraction was that of medium-sized and small particles, whereas in the coffee K2, medium-sized and large particles dominated. Also, the structure of the coffee K3 particles from $f > 2.5$ mm fraction was open and highly porous, while the particles of the coffee K2 from the $f > 2.5$ mm fraction was compact, with smaller pores. The K1 coffee's particles were regular, with briquette-like shape and compact surface, although that its sorptive capacity was relatively high. However, it is known that products obtained as a result of lyophilization are highly porous with consequently highly developed surface, which favours considerable sorptive capacity.

Supposedly, the v_m capacity was mainly determined by the production technology, involving not only the manner of dehydration, but also accompanying operations aimed at developing the product's structure (compactness and porosity). The compactness of surface and its porosity were probably those factors that determined the course of adsorption on the particles of the tested coffee brands.

The water activity corresponding to the monomolecular layer had the lowest value for the K1 coffee brand. Considering a large capacity of the K1 coffee, it can be supposed that changes during a storage period will be less intense in it than in the other two brands [Mathlouthi, 2001]. It refers the changes connected to an increase in the amount of free water in the product during storage time. In terms of the susceptibility to going rancid, caused by the presence of oxygen, lyophilised products are less durable than those dried in a conventional manner [Lorentzen, 1979].

The energy constant c which reflects the difference between the enthalpy of desorption from a monolayer and the enthalpy of evaporating of liquid adsorbent, for the process of physical adsorption adopts the value of about 20 kJ/mol. The enthalpy of chemisorption is much higher – up to about 200 kJ/mol. During the process of chemisorption, the particles are bound to the surface by chemical bonds. A slight change in enthalpy in a physical process does not usually affect the identity of the physically adsorbed particles. However, it must be borne in mind that the presence of a surface can cause their distortion [Atkins, 2003].

The results obtained in the experiment indicate that in this case, only a physical process took place. However, complete certainty can be obtained after spectroscopic tests have been performed.

The values of v_m were used to calculate the specific area of sorption. The results (Table 3) showed that that the K3 coffee brand had the highest specific surface. The degree of surface development allows for supposition that mesocapillaries were the dominant form of capillaries.

CONCLUSIONS

The sorption isotherms were sigmoidal in shape, which is typical of products of complex composition. The shape of the sorption curves indicated multilayer adsorption and porous structure of the tested products.

Adsorption of water vapours by the coffees increased with the growth of the a_w parameter. The coffee K3 showed higher equilibrium values of humidity in almost the whole range of a_w .

TABLE 3. Parameters of the BET equation for the tested coffee brands.

Coffee	v_m (g/g)	a_w (-)	c (kJ/mol)	a_{sp} (m ² /g)	RMS	r
K1	6.3044	0.1703	29.02	221.5	0.5334	0.9932
K2	5.0424	0.1880	31.03	177.2	1.8484	0.9561
K3	6.7225	0.2738	23.24	236.2	1.0618	0.9850

In addition, the highest monomolecular layer capacity, calculated from the BET equation, was found in K3, which resulted in the highest value of specific surface in this brand. However, in the lyophilised brand of the coffee K1, the monomolecular layer capacity was only slightly lower.

The water activity which corresponded to the monomolecular layer capacity had the lowest value for the coffee brand K1. The fact may mean that lyophilised coffee is more durable in storage, which is conditioned by processes depending on water activity.

The values of the energy constant in the BET equation indicated the physical ($\sim 10.3\div 19.7$) nature of the process.

Summing up, the tested coffee brands were different in terms of their sorptive properties.

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