

Przemysław Dmowski
Millena Ruszkowska
Gdynia Maritime University
Poland

STUDIES ON THE HYGROSCOPICITY OF SOME BLACK TEAS IN TERMS OF THEIR STORAGE STABILITY

The aim of the study was to evaluate the hygroscopicity of black tea samples in terms of storage stability based on the sorption kinetics determined by the dynamic and static methods for 48 hours. In order to describe empirically determined sorption isotherms, the equation of Brunauer, Emmett and Telleeta (BET) was transformed in the range of water activity $0.07 \leq a_w \leq 0.33$. The equation was characterized based on the correlation coefficient (R^2) and the fit standard error (FitStdErr). Based on extensive investigations, it was found that the higher storage stability characterized the tea from Indonesia, which may be due to differences in the microstructure of the surface resulting from the tea origin and parameters of the drying process.

Keywords: sorption kinetics of water vapor, sorption isotherm, BET isotherm, storage stability of tea.

INTRODUCTION

Tea belongs to the group of stimulants that have a beneficial physiological effect; it is obtained from the leaves of young, immature buds of deciduous shrub (*Camellia sinensis*). Tea is grown in countries with warm and humid climate, grown mainly in China, India, Japan, Sri Lanka, but also in Brazil, Argentina and Cameroon [1,6]. A critical parameter in determining the quality and storage stability of tea is content and water activity. Tea requires particular temperature, humidity and possibly ventilation conditions. In sea transport, tea belongs to the group SC VI (storage climate conditions VI), requires particular temperature, humidity and possibly ventilation conditions. This group includes goods with a low water content (2–4%), which is constantly determined by the humidity and temperature conditions of the ambient medium. The water content of black tea must not fall below 2%, as the product otherwise becomes hay-like and its essential oils readily volatilize, while on the other hand, it must not exceed 9% as it then has a tendency to grow mold and become musty. The sorption isotherms for these hygroscopic goods exhibit a continuous profile without sudden jumps. Undesirable changes occur as a function of relative humidity and temperature, in particular due to dampening (mold, rot, mildew stains, fermentation, deliquescence, self-heating) or desiccation (solidification, jamming/caking, fragmentation, drying-out). The goods

in this group do not have any particular requirements as to ventilation conditions, since they are dry for shipment and do not respire [17]. During transport of teas from many regions of the world, e.g., by sea, the product may be exposed to fluctuations in humidity, which can affect the growth of product hygroscopicity. Thus, an effective tool to determine the hygroscopic properties is to determine the sorption isotherms of water [4, 5, 11, 12], so it can be identified by the sensitivity of the product to moisture and predict changes that may occur in the material during storage [3, 15].

The use of adsorption isotherms as an indicator of the storage stability of the product is based inter alia on the basis of a calculation capacity monolayer (v_m), which corresponds to a single layer of molecules adsorbed water vapor. Excess water in relation to the monolayers leads to the exceeding of the critical moisture content, which can cause undesirable product changes [8].

1. MATERIAL AND METHODS

The four samples of black tea were obtained from China (tea I), Sri Lanka (tea II), India (tea III) and from Indonesia (tea IV). In the studied teas I-IV, initial content and water activity were set. Determination of water content was performed by drying at 103°C [14]. Determination of water activity were performed in a AquaLab Series 3 model TE (TE Series 3 model, the company Decagon Devices, USA), with an accuracy of ± 0.003 at 20°C.

The evaluation of the hygroscopic properties of a static method - carried out by determining the water vapor adsorption isotherms, the equilibrium humidity between the test sample and the atmosphere of defined relative humidity controlled using saturated salt solutions [11]. Determination of adsorption isotherms were performed at $20^\circ\text{C}\pm 1^\circ\text{C}$ in a range of water activity $a_w = 0.07-0.93$. Fixture time equilibrium was 90 days. The sample for the study consisted of about 2 g of the product tested. Based on the initial weight of the product and the growth or loss of water content equilibrium water content was calculated and plotted sorption isotherm.

In order to describe empirically designated sorption isotherms have been converted into the equation of Brunauer, Emmett and Tellea (BET) (1), the range of water activity $0.07 \leq a_w \leq 0.33$. The equation was characterized on the basis of the coefficient of determination (R^2) matches the standard error (FitStdErr).

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

where:

- a – adsorption (g/g);
- v_m – monolayer water content (g/g);
- c – constant energy (kJ/mol);
- a_w – water activity (-).

Characteristics of sorption properties included determination of monolayer capacity, specific surface adsorption, the total volume of the capillaries and the radius of capillaries undergoing filling the initialized capillary condensation on the basis of the Kelvin equation [9].

The specific surface area of the adsorbent was calculated based on equation (2) [10]:

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

where:

- a_{sp} – surface area of sorption (m²/g);
- ω – water setting surface (1.05·10⁻¹⁹ m²/molecule);
- M – water molecular mass (18.015 g/mol);
- N – Avogadro number (6.023·10²³ molecules/mol).

The kinetics of water vapor sorption were determined in the environment with relative humidity of – $a_w = 0.44, 0.69, 0.86$, within 48 h. Interpretation of sorption kinetics were kinetic curves, which represented graphic description of changes in the quantity of water (g/100 g d.m.) adsorbed over time.

2. RESULTS AND DISCUSSION

Based on the assessment, it was found that the obtained values of the initial water content of teas I-III, satisfied the requirements of the standards [14] and did not exceed the recommended content of 8%, which was consistent with the literature determining the water content in tea at the level of 4–18% [4] similar test results obtained by Plust et al. [13]. Only in tea IV (coming from Indonesia) initial water content exceeded the level of 8%, and showed the highest activity of water in the midst of the evaluated group of teas (Tab. 1).

Table 1. The water content of the tested products I–IV

Product	Mean water content [g/100 g d.m.]	SD [-]
I	6.623	0.0010
II	7.134	0.0004
III	4.974	0.0009
IV	8.496	0.0016

Abbreviation: SD – standard deviation

Source: Own study, (n = 3).

The physical, chemical and microbiological changes occurring in food products in each range of water activity differ in, however, the speed and intensity, thus ensuring appropriate conditions for storage ensures the quality of products

[16]. In the studied teas the lowest initial water activity was characterized by the tea III (0.266). On the basis of the initial assessment of water activity in the studied teas I-IV, it was found that the products were evaluated microbiologically stable (Tab. 2).

Table 2. The water activity of the tested products I-IV

Product	Mean water activity [-]	SD [-]
I	0.370	0.0059
II	0.427	0.0078
III	0.266	0.0143
IV	0.502	0.0120

Abbreviation: SD – standard deviation

Source: Own study, ($n = 3$).

Hygroscopic properties of teas I-IV are determined by comparing the relative positions of water vapor adsorption isotherms (Fig. 1). Sorption isotherms determined empirically in tested teas I-IV, were characterized by sigmoidal in shape and, according to the classification of Brunauer, showed similarity to the isotherms of type II. Designated sorption isotherms in tested teas I-IV, characterized by continuity in the course of the entire range of water activity (0.07–0.93) with increasing water activity increased water content in the analyzed teas I-IV. The use of adsorption isotherms as an indicator of the storage stability of the product is based inter alia on the basis of a calculation capacity monolayer (v_m), which corresponds to a single layer of adsorbed water vapor molecules [7, 8].

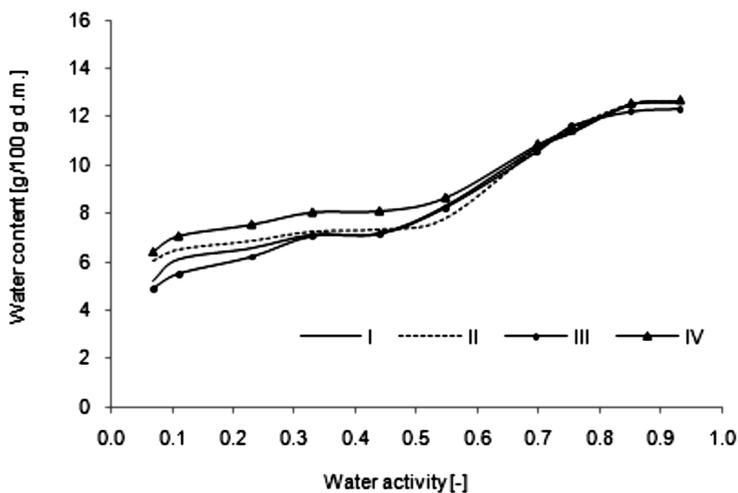


Fig. 1. Sorption isotherms of product I-IV

The course of sorption isotherms in the water activity range of $a_w = 0.07-0.33$ enabled determining parameters of the BET equation (v_m) by assaying the degree of its fit (R^2 , FitStdErr) to empirical data. Respective results were presented in Table 3.

Table 3. The BET equation parameters

Product	v_m	R^2	FitStdErr
I	4.75	0.996	0.452
II	4.77	0.980	0.596
III	4.74	0.982	0.151
IV	5.33	0.997	0.819

Abbreviations: V_m – monolayer capacity; R^2 – determination coefficient; FitStdErr – fit standard error

Source: Own study.

The studied teas I–IV were different in terms of size monolayer. The tea IV was characterized by the highest capacity monolayer. It can be assumed that water was bonded stronger in this type of tea than in other types. Probably, the cause of this situation were differences in the microstructure of the surface determined by the origin of tea IV and parameters of the drying process.

Table 4. Microstructural characteristics of the tested product I and II

Product	Specific surface of sorption a_{sp} (m^2/g)	Total capacity of capillaries ($mm^3/100 g$)	Size of capillaries at $a_w=0.70$ (nm)
I	166.81	36.47	2.40
II	167.74	36.64	2.43
III	166.37	36.09	2.45
IV	187.35	36.65	2.42

Source: Own study.

The volume of the capillary of tested teas I–IV was estimated to be the sum of the volume of water adsorbed by the material in the water activity range from 0.75 to 0.93. Determination of the total volume of the capillaries in the area of capillary condensation, based on the progression of sorption isotherms at $a_w = 0.75$ (Tab. 4) showed that the highest values of the rated parameter were characterized by a product. It can be assumed that the chemical composition of the product determines the differentiation capacity of the capillaries. Resolution of the most probable radius of the capillary in the tested teas I–IV ranged from 2.40 to about 2.45 nm.

The kinetics adsorption is the study on the speed of the adsorption process. The dependence of the increase of water content as a function of time is called the kinetic curve and is the basis for the interpretation of the sorption of water vapor by the product. The use of dynamic measurement of water vapor adsorption for food products has a number of advantages as compared with the static method. It allows you to shorten the determination and gives you the ability to analyze multiple factors influencing the speed of the process [2].

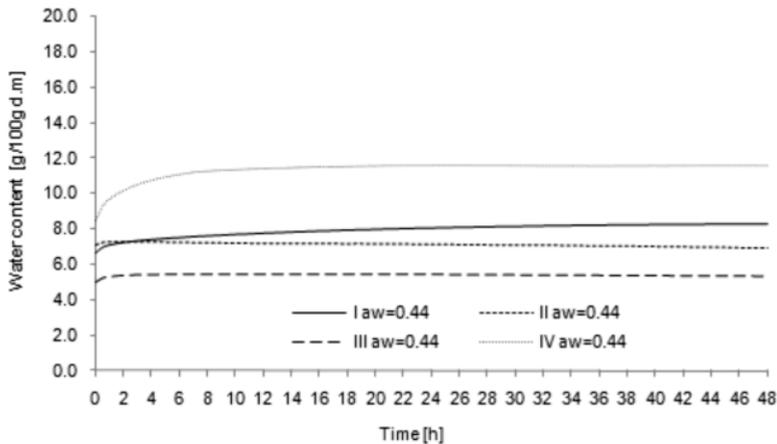


Fig. 2. The vapor sorption kinetics of product I–IV, in an environment with a water activity of $a_w = 0.44$

The kinetics of adsorption of water vapor in the tested teas I–IV is set out in a medium of water activity $a_w = 0.44, 0.69$ and 0.86 (Fig. 2–4).

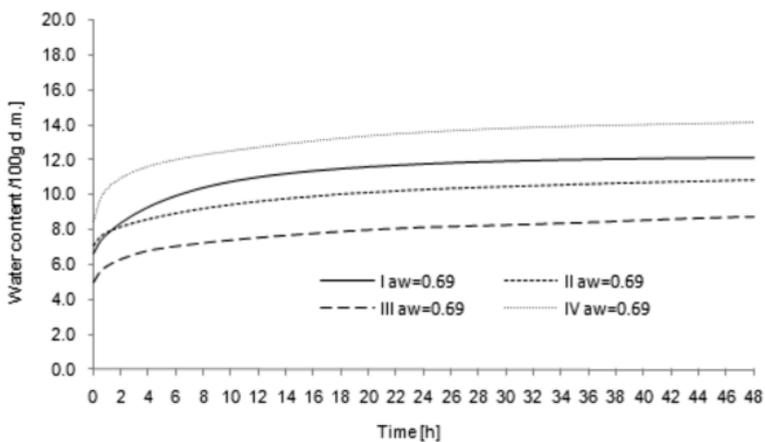


Fig. 3. The vapor sorption kinetics of product I–IV, in an environment with a water activity of $a_w = 0.69$

It was found that the curves of kinetics of water vapor sorption of the teas I–IV developed similarly and their progress was conditioned by the initial water content in the assessed teas. Differences moisture of the product and its environment depends on the moisture potential difference and determined the power of the processes [16].

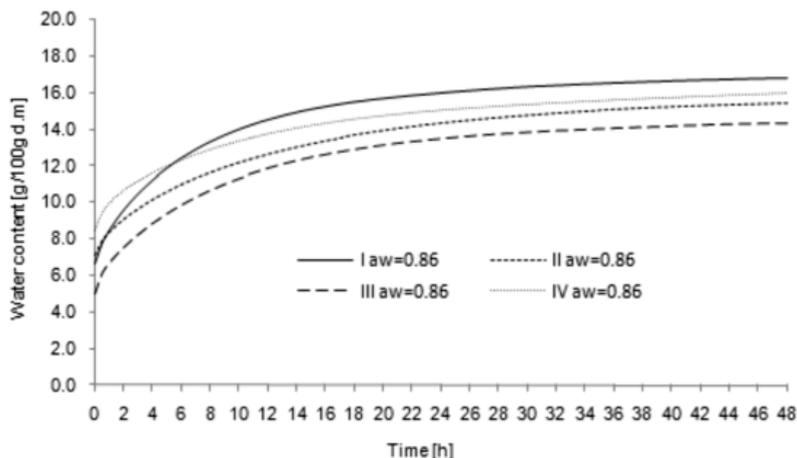


Fig. 4. The vapor sorption kinetics of product I–IV, in an environment with a water activity of $a_w = 0.86$

CONCLUSIONS

1. The sorption isotherms of water vapor surveyed teas characterized by a sigmoid course compatible with type II sorption isotherms according to the classification of Brunauer.
2. In assessing the progress of individual sorption isotherms of water vapor it was found that strong hygroscopic properties characterized the tea from Indonesia.
3. The tea from Indonesia was characterized by the higher capacity monolayer and the most preferred sorption properties.
4. On the basis of evaluation of dynamic sorption process, it was found that the tested teas in each case endeavor for obtaining equilibrium humidity of the surrounding atmosphere and the driving force for the humidity was the potential difference between the test product and the environment.

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