

VERIFICATION OF POTENTIAL THEORY OF ADSORPTION
IN DETERMINING FOOD SORPTION ISOTHERMS

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Abstract. The aim of the thesis is the evaluation of possibilities of application of the Polanyi adsorption potential theory for calculation of food sorption isotherms. The test material were instant type soup concentrates and fragmented pasta. Applying the static-desiccator method, the tested material sorption isotherms were defined, at temperatures of 20°C and 30°C. Next, on the basis of the isotherms empirically defined at the temperature of 20°C, the isotherms at 30°C were calculated using the potential theory of adsorption (PTA). The evaluation of the efficiency of PTA was made by comparison of the location of the empirically defined and theoretically calculated sorption isotherms for 30°C. The results received showed that the complexity of the composition and of the structure of food constitutes a serious limitation to the PTA efficiency. PTA may be applied in calculation of isotherms of sorption of food with homogeneous composition and ordered, stable structure.

Key words: potential adsorption theory, food concentrates, evaluation of efficiency

INTRODUCTION

The potential theory of adsorption by Polanyi is based on the assumption of existence of equipotent adsorption layers on solid body and serves for the determination of sorption isotherms at various temperatures. The potential theory of adsorption does not define the equation of the adsorption balance. The potential theory of adsorption (PTA) allows to calculate the adsorption isotherm at T_2 temperature on the basis of the isotherm at T_1 and the values of liquid density ρ and the values of the balancing pressure p over a pure liquid in T_1 and T_2 [4].

Satisfactory results of verification of the effectiveness of potential theory of adsorption would enable practical application of the theory with regard to food for the testing of quality changes in foodstuffs in the case of storage in diversified conditions without the need to perform long-lasting and expensive research.

PURPOSE

The purpose of the study was to determine the accuracy with which potential theory of adsorption allows us to foresee sorption isotherms under new thermal conditions.

With reference to the purpose, sorption isotherms were determined empirically at temperatures of 20°C (E20) and 30°C (E30), and the course of the curve was determined with the application of PTA at 30°C (T30). Comparison of the position of the sorption isotherms determined for 30°C empirically (E30) and theoretically (T30) made it possible to verify PTA effectiveness with regard to food.

RESEARCH MATERIAL

A group of foodstuffs which are dry and regarded as concentrated food was the research material. As a result of the applied technological process, the said products are characterized by strong affinity to water and by interaction with climate through having a raised humidity. The products were assigned the following symbols:

- IA – as being a true solution (beetroot soup),
- IB – as being a colloidal solution (pea soup),
- IIA – as being a true solution (beetroot soup),
- IIB – as being a colloidal solution (pea soup),
- MB – as being subject to swelling (egg-free pasta),
- MS – as being subject to swelling (6-egg pasta).

In Table 1 the composition of the raw materials and the chemical constitution of the tested products is presented.

Table 1. Raw material composition and chemical constitution of tested products

Product	Raw material composition	Parameter	Value
Red beetroot soup IA	Dried concentrated red beet juice (42%), concentrated juice from beets, maltodextrine, sugar, salt, vegetable hydrogenated fat, taste- and smell-strengthening substances: monosodium glutamate, yeasty dried extract, acidity controllers: citric acid, sodium diacetate and lactose, natural aroma, anticaking substance E551	Energetic value kJ (kcal)	98.8(23.6)/100ml
		Protein	0.4 g/100ml
		Carbohydrates	4.6 g/100ml
		Fat	0.4 g/100ml

Table 1. Cont.

Beetroot soup IIA	Sugar, dried concentrate red beet juice, croutons, salt, natural aroma, taste- and smell- intensifying substances (E621, E635), acidity controllers (E330), spices, vegetable fat, identical with natural aroma	Energetic value kJ (kcal)	284 (68)/portion
		Protein	0.9 g/portion
		Carbohydrates	12.0 g/portion
		Fat	1.8 g/portion
Pea soup IB	Pea flour (57%), wheat croutons (8%), potato starch, salt, vegetable hardened fats, roasted smoked bacon (4%), substances strengthening taste and smell: monosodium glutamate, sodium inozinian, sodium guanyl, spices: garlic, marjoram, pepper and glucose, dried yeasty extract, aroma	Energeticvalue kJ (kcal)	168(40)/100ml
		Protein	1.9 g/100ml
		Carbohydrates	5.4 g/100ml
		Fat	1.2 g/100ml
Pea soup IIB	Steam pea flour, croutons, vegetable fat, salt, substances strengthening taste and smell (E621, E635), maltodextrine, natural aroma, yeasty extract, dried onion, food thickeners E412, spices, food colours (E150c, E101)	Energetic value kJ (kcal)	360(86)/portion
		Protein	3.1 g/portion
		Carbohydrates	10.9 g/portion
		Fat	3.3 g/portion
Egg-free pasta	Semolina from Canadian Amber Durum N*1 wheat, water	Energetic value kJ (kcal)	1519(363)/100g
		Protein	12.9 g/100g
		Carbohydrates	73.50 g/100g
		Fat	1.86 g/100g
6-egg pasta	Semolina from Canadian Amber Durum N*1 wheat, fresh eggs (6 eggs per 1 kg of semolina), water	Energetic value kJ (kcal)	1600(382)/100g
		Protein	16.1 g/100g
		Carbohydrates	70.55 g/100g
		Fat	3.98 g/100g

Source: own juxtaposition of products to be tested on the basis of data given on labels.

METHODS

In order to determine empirically the course of sorption isotherms, the static-desiccator method was applied at the range of 0.07-0.98 water activity and temperatures of 20°C and 30°C [6,7].

On the basis of characteristics applied in determining the sorption isotherms for saturated salt solutions, the molar adsorption potential A was calculated. The said value which is the relation of molar free energy connected with the change of the equilibrium pressure over a pure liquid phase p_0 to the pressure p of molar free energy being in the equilibrium with the quantity adsorbed of substance a is characterised by the equation:

$$A = RT \ln \frac{p_0}{p} \quad (1)$$

where:

A – molar adsorption potential (J kmol^{-1}),

R – universal gas constant (J (kmol K)^{-1}),

T – temperature (K),

p_0 – saturated vapour pressure at T over the level of pure liquid adsorbate (Pa).

p – adsorbate vapour pressure over adsorbent (Pa).

Adsorbate volume on the adsorbent surface in relation to the unit mass of the solid body (W) is determined using the equation as follows:

$$W = \frac{a}{\rho_c} \quad (2)$$

where:

W – volume of adsorbed substance in relation to adsorbent unit mass ($\text{m}^3 \text{ kg}^{-1}$).

a – adsorption (kg kg^{-1}).

ρ_c – adsorbate density (kg m^{-3}).

Bearing in mind the fact that in the case of using the lower thermal ranges of adsorption – (20°C and 30°C) the temperature of sorption was definitely lower from that of the boiling point of adsorbate under the normal pressure (100°C), it is known that the surface layer is the liquid [4].

RESULTS AND DISCUSSION

The verification of PTA effectiveness was based on the estimation of the quality of adjustment of the model (T30) to experimental data (E30) (Fig. 1).

For this purpose the following characteristics were used:

- dispersion as the range between calculated and experimental adsorption values in the individual points [2],
- correlation between calculated and experimental adsorption values in the individual points [2],
- quantity reflecting the area which is determined through the T30 model and empirical E30 data in the field of incongruity.

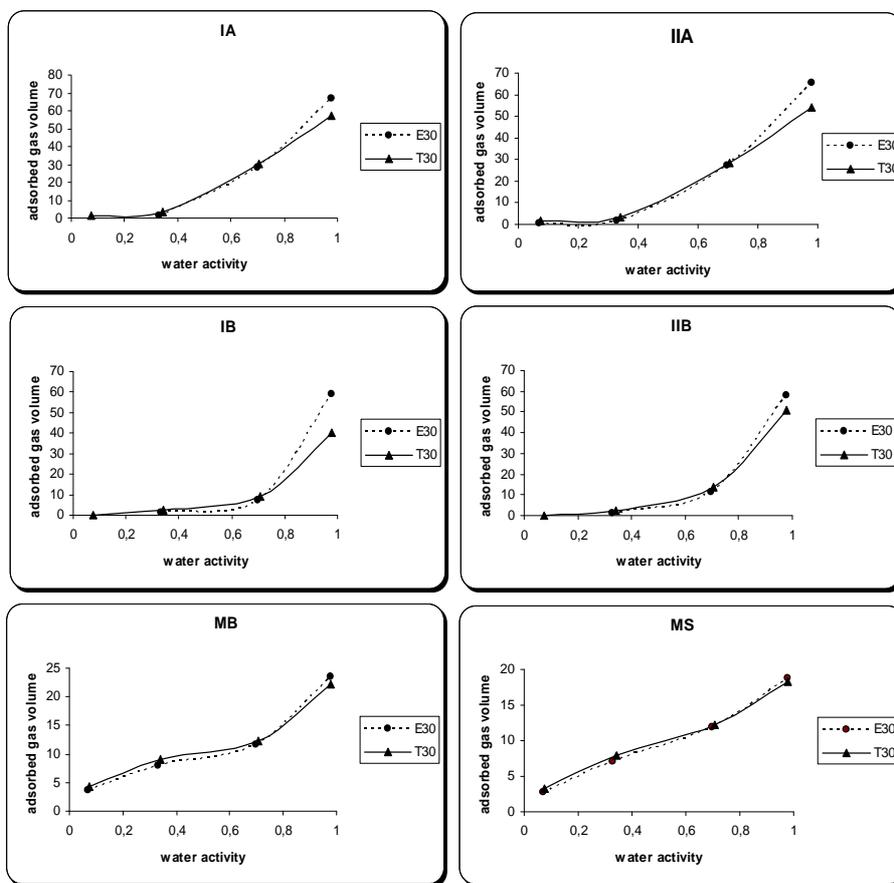


Fig. 1. Correlations between sorption isotherms at 30°C determined empirically (E30) and calculated theoretically for 30°C (T30)

The dispersion values obtained are presented in Table 2.

Table 2. Dispersion between theoretical and empirical values of adsorption in determined conditions of humidity

Product	$p \cdot 10^{-3}$ (Pa)	R_i	R_x	S	S^2	V(S)
IA	163.1	–				
	771.9	1.181	4.106	4.321	28.00	105.2
	1632	0.921				
	2288	10.21				
IB	163.1	–				
	771.9	0.830	6.949	8.498	108.3	122.3
	1632	1.051				
	2288	18.97				
IIA	163.1	1.327				
	771.9	0.769	3.533	4.413	25.96	124.9
	1632	0.869				
	2288	11.17				
IIB	163.1	–				
	771.9	0.783	3.201	2.948	13.04	92.10
	1632	1.476				
	2288	7.355				
MB	163.1	0.448				
	771.9	1.111	0.858	0.391	0.204	45.62
	1632	0.507				
	2288	1.365				
MS	163.1	0.323				
	771.9	0.757	0.504	0.187	0.046	37.01
	1632	0.328				
	2288	0.611				

Source: own juxtaposition

R_{ib} – point range,

R_x – average range,

S – standard deviation,

S^2 – variance,

V(S) – coefficient of variation.

The analysis of dispersion effects shows that the point range was heterogeneous for the individual products. In the case that the products after rehydration became solutions (true and colloidal), the average values of the point range were higher in comparison with the products which are subject to swelling only and resulting from significantly full rehydration. Particles constitute the mixtures IA, IIA, IB and IIB which were characterized by a variety of their compositions and structures. The MB and MS, however, were a definitely homogeneous setup. Their dominating component was starch. It may be assumed that the complexity of the composition and the structure of the product is the significant factor influencing the effectiveness of PTA in determining sorption isotherms.

Moreover, in the case of products which are solutions (values of the standard deviation, the variance and the coefficient of variance) there were considerable differences in the range of points, which was not found in the case of products which are subject to swelling. At the points of low value p the said range of points for each sample to be tested were of low values. This may suggest the fact that PTA can create a good isotherm of sorption within a narrow range of a_w only.

Correlations of points between calculated and experimental values of adsorption were presented for each tested product in the form of the correlation diagram (Fig. 2).

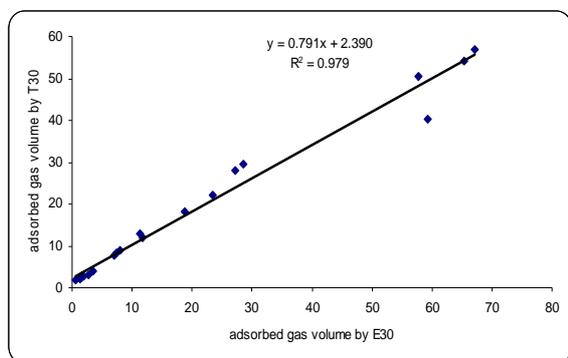


Fig. 2. Correlation diagram

Preliminary analysis of the correlation diagram proved the existence of the positive linear correlation. The linear equation was determined with the least squares method. This equation was the best representation of the preceding correlation. The straight line was characterized by a high value of Pearson's ratio ($r(xy) = 0.989$), which should be interpreted as significant interdependence between the values of adsorption which were determined on the basis of empirical data (E30) and of the model (T30).

Specification of the value of fields of incongruity was the last element of the estimation of convergence of the model with empirical data. For this purpose two-dimensional geometry has been used to determine the surface of curvilinear areas included in the range between considered curves from a_w 0.07 to 0.98. The combination of the results obtained is presented in Table 3.

Table 3. Juxtaposition of values of the fields of incongruity

Product	Value of the field			
	X	S	S ²	V(S)
IA	1.823	0.010	$1.00 \cdot 10^{-5}$	0.561
IB	3.057	0.034	$2.00 \cdot 10^{-4}$	1.126
IIA	2.564	0.023	$6.00 \cdot 10^{-5}$	0.884
IIB	2.004	0.004	$2.44 \cdot 10^{-5}$	0.221
MB	0.107	0.003	$1.21 \cdot 10^{-5}$	2.917
MS	0.198	0.001	$2.36 \cdot 10^{-5}$	0.694

Source: own juxtaposition.

X – average surface of field,

S – standard deviation,

S² – variance,

V(S) – coefficient of variation.

The sorption isotherm is a representation of the correlation between the quantity and the state of water contained in the substance under determined constant thermal conditions [3,4]. A change in thermal conditions causes the creation of a new isotherm whose position is the consequence of the influence of thermal energy on the state of water contained in the product. Such change in temperature may also be accompanied by a change of product's structure. The said type of changes occur especially easily when the structure of the product is characterized by amorphousness [1,5].

The results obtained show that the samples marked with MB and MS are characterized by the smallest values of fields of incongruity, thus the tested model proved to have the position of isotherms with the biggest sorption accuracy for both MB and MS products.

The MB and MS products, as a result of deep drying of starch prior to the subjection to rehydration, were characterized by crystalline and relatively stable structure of particles. An increase in temperature caused only change of the state of water (increase in its activity) contained in the product, resulting, consequently, in a change of the position of the isotherm. The structure of the tested products remained invariable, therefore it made the shape of the theoretical curve to be similar to the empirical one.

Sorption isotherms of the mixtures are a result of sorption isotherms of components of the mixtures. Both IA and IIA products resulted from spray-drying process of the decoction from beets and filling the resultant powder in with the supplement of substances improving the taste, characterized by the presence of components of low-molecular and twofold structure. The structure of powder from the reduction of decoction of beets was amorphous, which resulted from quick dehydration. However, crystalline structure was characteristic for applied substances for improving the taste.

Both IB and IIB products resulted from spray-drying process of the decoction earlier prepared on the base of pea, in which starch was subjected to the process of enzyme modification and filling substances improving the taste in with the supplement were characterized by the presence of components of low- and high molecular weight and various grade ordering.

Due to the interaction of increased temperature in the products IA, IIA, IB and IIB, the water activity was rising on the one hand and resulted in a change of the position of the sorption curves. On the other hand, the possible transformations of particles of labile amorphous structure may have taken place. In consequence, the shape of sorption curves also underwent a modification. Some suppositions may be made that the considerable values of fields of incongruity of such products as IA, IIA, IB and IIB were the consequence of structural transformations constituting the composition of some particles. Each time, however, the value of the field of incongruity was the bigger the more the shape of the theoretical and empirical curve was diversified.

CONCLUSIONS

1. To sum up, it is to admit that the tested model enabled the determination of the position of the sorption isotherms within the new value of temperature, complying with the conditions of exothermic process. The accuracy with which the model represents the position of the new isotherm was conditioned mainly by the chemical composition and the structure of the tested samples. The more complicated and diversified the samples tested, the less accuracy of the mapping may be assured. The curve of isotherm segments in relation to high values of vapour pressure over the solution were especially sensitive to distortions.

2. The isotherms determination procedures by using the basis of knowledge of one isotherm of the adsorbent have a very important meaning for chemical engineering. Its positive verification for various adsorbents that find application in chemical engineering made it possible to formulate the hypothesis about the chance to apply PTA in calculating isotherms adsorption of foodstuffs.

3. However, verification carried out on PTA effectiveness in determining sorption isotherms showed that the complexity of the composition and the structure of food is a serious limitation in the practical usage of PTA.

4. The final conclusion is that PTA may be able to find an application in calculating sorption isotherms of foods characterized by homogeneous composition and ordering, with a relatively stable structure. The PTA application in determining sorption isotherms of foods characterized by various compositions and labile structure may lead to a significant increase in errors in reflecting the position of sorption isotherms, especially in the field of maximum values of a_w .

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WERYFIKACJA SKUTECZNOŚCI POTENCJAŁOWEJ TEORII ADSORPCJI W WYZNACZANIU IZOTERM SORPCJI ŻYWNOSCI

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Streszczenie. Celem pracy była ocena możliwości zastosowania potencjałowej teorii adsorpcji Polanyi'ego do obliczania izoterm sorpcji żywności. Materiałem badawczym były koncentraty zup typu instant oraz rozdrobniony makaron. Stosując metodę statyczno-eksykatorową empirycznie wyznaczono izotermę sorpcji materiału badawczego w temperaturze 20°C i 30°C. Następnie na podstawie empirycznie wyznaczonych w 20°C izoterm obliczono za pomocą potencjałowej teorii adsorpcji (PTA) izotermę w 30°C. Oceny skuteczności PTA dokonano poprzez porównanie położenia wyznaczonych empirycznie i obliczonych teoretycznie izoterm sorpcji dla 30°C. Uzyskane wyniki wykazały, że złożoność składu i struktury żywności stanowi poważne ograniczenie w skuteczności PTA. Potencjałowa teoria adsorpcji może znaleźć zastosowanie w obliczaniu izoterm sorpcji żywności o jednorodnym składzie i uporządkowanej, stabilnej strukturze.

Słowa kluczowe: potencjałowa teoria adsorpcji, koncentraty spożywcze, ocena skuteczności