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SORPTION ISOTHERMS OF MILK MIXTURE

The article contains a brief description of water activity determination. The impact of water activity on the humidity of the food and it affecting microbial cells are described. Definition and classification of sorption isotherms with a brief description of each type are considered. Sorption isotherms of food materials are generally in sigmoid shape. There are given for each type of sorption isotherms the examples of products that lead the type. Sorption isotherms for products with high humidity are shown.

The technology of sample preparation and the experiment conduction are described in detail. It is analyzer Roremeter RM-10 was used in the work. The analyses of inert fillers like cellit powder, which are used when liquid samples, is given. The freezing point of the milk product was measured for liquid (not thick) solutions. Humidity measurement of native samples were carried out by express method with hygrometer Radwag.

The initial values of water activity, the freezing temperature, and humidity of the native samples of powdered milk and sterilized milk are given. The sorption isotherms of dairy product of various fat content, when it is produced with sterilized milk or distilled water, are shown. The conclusions about contribution in type of sorption isotherm of sample and it components internals are given.

Key words: water activity, freezing point, sorption isotherm, milk, diary product.

Introduction. Humidity control of materials, which is required typically by standards, serves for evaluation of product stability during storage, and its result impacts in technology to reach the desired properties. Excessive moisture of raw materials or products leads to inadequate price and it could be a way of a product adulteration. The term of “water activity” (A_W) was introduced to describe the contribution of moisture to damage of food products. Water activity reduces breaks, all types of spoilage reactions and growth of microorganisms, and stops them at a certain level of A_W. Exception is the chemical oxidation of lipids that is not concerned with microbiology directly. However, microbial cells survive even under law A_W, although they don’t demonstrate their vital activity.

Water activity in food is in equilibrium with the relative atmosphere humidity. If the relative humidity is less than the water activity in the product, the free moisture will evaporate from the product into the surrounding atmosphere. Otherwise, products absorb water from the air. If you put in this isolated system a milk product, an equilibrium moisture will be established in course of time. In this instance, the water activity value in the product becomes equal to the relative humidity level in the isolated system [1].

According to the level of water activity it is possible to divide products into their groups with high moisture (A_W = 1.0–0.9), intermediate moisture foods (A_W = 0.9–0.6) and products with low moisture (A_W = 0.6–0.0) [2].

Data on the moisture content in a food product may be represented as the ratio of moisture loss after drying to the amount of dry matter in the product (g of H_2O / g of dry matter), or as the ratio of moisture loss after drying to the total weight of the product for drying (g of H_2O / g of original sample weight before drying) [2]. Usually, standards define dairy humidity as the ratio of weight loss after the product drying to the weight of the product before drying. This method allows clear demonstrating the changes of product moisture during the drying process. The relationship between moisture content in the food product with the activity of water in it at a constant temperature is called a sorption isotherm. The information they provide with is useful to evaluate the processes of drying, mixing, packing, concentrating and dehydrating as well as to estimate the stability of the food product during storage [2, 3].

There are three types of adsorption isotherms that are shown at Fig. 1. Sigmoid (type II) waveform is the most extended among them [3].

Type I sorption isotherms are observed in pure crystalline sugar. In the area of water activity values up to 0.7–0.8 of figure 1 shows low moisture content, because the only hydrogen bonds of water with OH-groups of carbohydrates are presented on the surface of sugar crystals. Moisture starts to penetrate into sugar crystals with the increase of water activity that convert them into solution [3].

Type III appears in non-caking additives isotherms. In these substances, the binding energy is so great that water activity is suppressed while the water is absorbed. When binding capacities are filled the increase of humidity causes a sharp rose of the value of water activity.

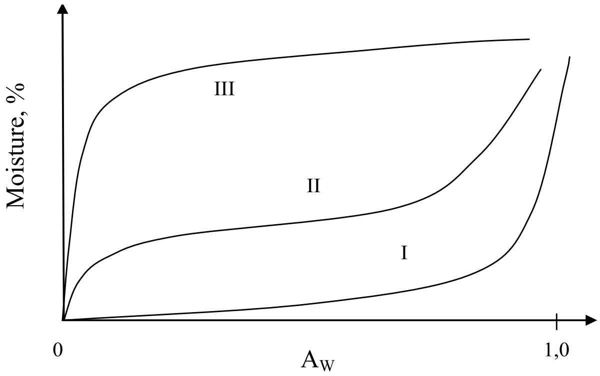

Fig. 1. Classification of the standard sorption isotherms

Some authors image a sorption isotherm for high moisture products in a view of Fig. 2 and label it as type I curve [2].

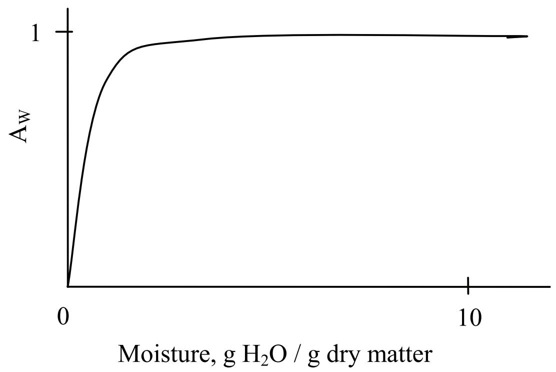

Fig. 2. Sorption isotherm for high moisture products

There are three specific zones (Fig. 3) in the sorption isotherms. Zone I corresponds to the most strongly bound water. It is unable to be a solvent, and it is not present in significant quantity to affect the softness properties of solid; water is just a part of it. It includes chemically bound water and monomolecular water layer that consists of associated polar group, which corresponds to a residual moisture after final product drying [1, 2].

Zone II is shaped by the immobilized water, the water molecules of a monomolecular layer, as well as distant adsorbed layers. The water in the zone II is the mixture of water of zone I and added water (resorption). Mostly, this water does not freeze till –40°C. This water contributes in the process of dissolution, it acts as a plasticizing agent and conduce swelling of the solid matrix. Water of zones I and II takes usually less than 5% of the total moisture in high moisture samples [1, 2].

Water of zone III contains a lot of added and weak bound water that is the most mobile one. In cellular systems or in gels it is bound physically, so its macro flow is aggravated. Water that is added from zone III freezes; it could be a solvent that is important for chemical reactions and microbial growth. Moisture of zone III (no matter if it is free or stated in macromolecular matrix) could amount over 95% of the moisture in high-moisture materials [1, 2].

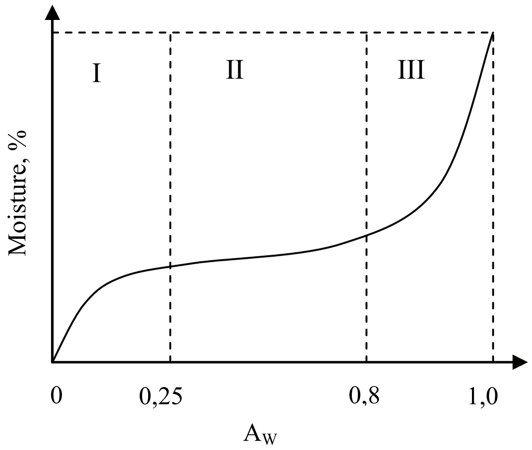

Fig. 3. The general waveform of a water sorption isotherm of a food product

According to [1] under a low level of A_W there are first of all milk proteins that are binding water. Within the A_W interval of 0.35 to 0.50, amorphous lactose absorbs water and turns into α-lactose (its hydrated form). These result in a sharp sorption decline at the surface. When A_W is > 0.60, water sorption begins mostly by low-molecular substances.

So, dairy products require high dryness to reduce significantly their water activity. Therefore, the sorption isotherms for milk concentrates and particularly for dry foods are of great practical importance [1]. Nevertheless, it is the shortage of published data on sorption isotherms for dried milk and affection of moisture.

Main Part. The following samples of domestic dairy products manufacturers were chosen as the objects of study:

– skimmed milk powder “Standard” with a fat mass fraction, which does not exceed 1.5%, and milk powder “Extra” with a fat content of 25%;

– UHT drinking milk with 1.3% mass fat content.

The sample preparing included the following steps. A weighed sample of milk powder was placed in a 100 cm^3 flask and poured by distilled water or sterilized milk. Samples within closed flasks were vigorously shaken and left undisturbed for at least 12–14 hours to establish equilibrium moisture content of the samples.

Analysis of free water fraction was run by the method of the dew point measuring at a chilled mirror that was realized with the water activity analyser Roremeter RM-10 by company NAGY Messsysteme GmbH. Sample freezing temperature was determined by the freezing point depression method with milliosmometre-cryoscopes thermoelectric MT 5-01 (Burevestnik, St. Petersburg).

Measurements of moisture and dry matter content of samples of milk powder and UHT milk were carried out by the accelerated method with a device Radwag (Poland), where using the dried filter paper was used as sample carrier. It was selected the standard drying profile under drying temperature of 125°C and automatic shutdown when the mass loss is less than 1 mg per 120 s.

The accuracy of due point measurement was 0.01°C, freezing point ±0.004°C, the accuracy of the weight measurements was no worse than 1 mg.

Determination of intermediate moisture values and dry matter of dairy products was carried out by calculation taking into account the weight of the sample used. The results for two samples of any of all three products are shown at Table.

Moisture average values for dairy products

Matter of sampls	Moisture of samples, %	
	I	II
Dried milk	2.61	2.68
Fat free dried milk	4.35	4.55
Sterilized drinking milk	90.33	90.30

Freezing temperature means for two samplers of sterilized drinking milk were –0,526°C and –0,510°C.

The product remained powder under water content below 50%, than it became into highly viscous paste, and under water content over 60% it changed into liquid.

The sorption isotherms of all the dried dairy products were of type I. Fat of samples did not affect A_W value. The share of strong bound moisture was found to be small enough and correspond to the residual moisture by milk drying taking into account water resorption from the introduced liquids. Therefore, zones I and II are extremely narrow bands and transform with liquid milk adding into zone III, when the product becomes liquid. After this one can observe the plato of A_W at its value is close to 1. These results correspond to the earlier received in [1–3].

Conventional liquid milk is a high moisture product with A_W over 0.9. This resulted in the same waveforms of sorption isotherms for two used as the solvent liquids and different started moisture of dried milks samples. Nevertheless, there could be some features. For example, the curves are obtained to be shifted in the area of law moistures for the samples with lower initial water content. For moistures over 30% it was insignificant.

When moisture dairy product is over 60% it became possible to determine its freezing point. It was found this temperature directly depends on the moisture content. At the same time, the received lines for used dry milk (skimmed or conventional) with different solvents are close to be parallel. No apparent relationship between freezing point temperature and water activity values was observed. Probably, it was due to the dependence of freezing point on the moisture content of the product and, as well, on the amount of carbohydrates and mineral salts that have the greatest impact.

Conclusion. It was found that sorption isotherms are similar for dried skimmed milk, and diluted powdered milk of 25% fat content. The solvent origin (distilled water or sterilized milk) does not affect the observed lines. Under high moisture, the curves belonged to type I.

Moreover, the character does not affect the components of the curve of the finished drinking water sterilized milk or the difference in moisture content between the heat-treated milk and distilled water. The curve of the type I is for products with high humidity. When A_W is >0.60, the effect of water sorption significantly affects the shape of the curve.

The experiments' results demonstrated the direct of freezing point from the moisture content in the dairy products. The apparent relationship between the freezing point temperature and the water activity value was not observed.

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