RESEARCH ARTICLE

Moisture adsorption characteristics of sandesh powder

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Abstract: Sorption studies were carried out for sandesh powder at 10°C, 20°C and 40°C to determine its moisture adsorption characteristics. The adsorption curves obtained were observed to follow a sigmoid shape and corresponded to type II, with a definite inversion due to the temperature effect above 0.79 water activity. The GAB, BET and Caurie isotherm models were attempted to describe the experimental data and were found to give the best fit as indicated by %RMS and R² values. Monolayer moisture content was calculated using the BET and GAB model. Caurie model was used to compute the properties of sorbed water viz., monolayer water, number of adsorbed monolayer, density, and surface area of adsorption in sandesh powder. The net isosteric heat of sorption of water in sandesh powder estimated using Clausius-Clapeyron equation at different moisture contents indicated its strong dependence on moisture content.

Key words: Sandesh powder, water activity, equilibrium moisture content (EMC), sorption isotherms, mathematical models

Introduction

Sandesh is the most popular chhana based sweet delicacy prepared in India and specially known as Bengali sweet. Sandesh is popular for its palatability, aroma and rich source of milk proteins, fat, sucrose and fat soluble vitamins. It has a firm body and smooth texture (Aneja et al., 2002). In spite of wide popularity and increasing market in India and abroad, the scope for organized marketing of sandesh is limited due to lack of systematic packaging and shelf life studies. For ready to eat and instant food formulations data on equilibrium moisture content of dried product is needed. Therefore the sorption studies were carried out for sandesh powder at 10°C, 20°C and 40°C to determine its moisture adsorption characteristics.

Several empirical, semi empirical and theoretical models have been reported for mathematically assessing moisture sorption isotherms of foods by Boquet et al., 1978; Chirife & Iglesias, 1978; Van den Berg & Bruin, 1981. Different properties of sorbed water could be obtained from the model proposed by Caurie (1981). The knowledge of temperature dependence of sorption phenomenon provides information for modeling and thermodynamics of the system. The model such as Brunauer, Emmett and Teller (BET) and Guggenheim-Anderson-deBoer (GAB), suffers from the non inclusion of temperature dependence relationship directly, though it is important in the model coefficients.

The isosteric heat of sorption ($q_{st}$), or differential enthalpy of sorption yields a measure of water-solid binding strength via intermolecular attraction forces between the sportive sites and sorbet and it is greater than the latent heat of vaporization of pure water at a particular temperature. The change in $q_{st}$ with the change in moisture content of the sample indicates availability of polar sites to water vapor as desorption/adsorption proceeds (Chung & Pfost, 1967). The isosteric heat of sorption can be estimated from the isotherms at two or more temperatures by using Clausius-Clapeyron type equation.

Sorption isotherms of several food products including whey protein, casein, lactose, whey powder, milk powder, cheese and yoghurt have been established, but the published report on indigenous dairy products are scarce. Information on moisture sorption isotherms of indigenous dairy products including Peda (Biradar et al., 1985), Chhana powder & Casein (Bandyopadhyay et al., 1987), Khoa (Sawhney & Cheryan, 1988), Daudh churpi (Hossain et al., 2002), Kheer (Jayendra Kumar et al., 2005), Chhana podo (Rao et al., 2006.), Curd powder (Varghese et al., 2008), ready to use Basundi mix (Sharma et al., 2009) and Banana shrihand (Quadri et al., 2015) have been reported. However, the data on moisture adsorption characteristics of sandesh powder was limited. Both adsorption and desorption isotherms are
necessary depending upon particular task in hand (Varghese et al., 2008). The information is useful to understand re-hydrational properties, drying conditions, packaging and to develop ready to eat and ready-to-use product.

The objective of this study was to determine the moisture adsorption characteristics of sandesh powder in the temperature range of 10 to 40°C, to examine the applicability of sorption models, to estimate the properties of sorbed water and to calculate heat of sorption.

Materials and Methods
Preparation of Sandesh

Good quality cow milk obtained from local market and standardized to 3.5% fat and 8.5% SNF was used for preparation of sandesh. Initially milk was heated to 90°C and cooled to 70°C. The hot milk was coagulated by using 1% solution of citric acid as an acidulant previously heated to the milk temperature, adding and stirring gently without breaking the coagulum formed till the clear whey appeared. The precipitation of milk involves the formation of large structural aggregates of protein. The whey formed during the process was removed by draining it through the muslin cloth by hanging the mass till the dripping of the whey ceased. The chhana obtained was kneaded in smooth paste, mixed thoroughly with addition of refined well ground cane sugar at the rate of 30% of the weight of chhana (Singh et al., 2006) and cooked at 75°C for 15 minutes over a low flame with constant scrapping until the mixture attained desired consistency and typical cooked flavor (Aneja et al., 2002).

Preparation of sandesh powder

In order to prepare dried product for adsorption studies, the sandesh obtained was passed through REMI laboratory blender to generate thin paste with uniform consistency. The product was spread in thin layer over a clean and dry aluminum tray. The tray was placed uncovered on a hot water bath to facilitate removal of visible free moisture. After thirty minutes, tray was removed, its bottom wiped and transferred to well ventilated oven set initially at 40°C. Drying was carried out in an oven for 48 hrs. The final drying was carried out in a desiccators over a week using concentrated sulphuric acid (H₂SO₄) as desiccant. The proximate compositional analysis was carried out as per standard methods (ISI, 1981 and AOAC, 2005).

Sorption set up

The sorption set up as recommend by Wolf et al., 1985 was used for establishing the moisture sorption isotherm and equilibration studies. It consisted of sorption containers and support for weighing dish in which sample was exposed to humid atmosphere in an air tight assembly. Each sorption container represents specific relative humidity. For temperature control sorption containers in duplicate measure were placed in the thermo-regulated chamber maintained at 10°C, 20°C and 40°C.

Ten reagent grade salt solutions in the water activity range of 0.11-0.97 as recommended by Greenspan (1977) viz., lithium chloride (LiCl), potassium acetate (CH₃COOK), magnesium chloride (MgCl₂), potassium carbonate (K₂CO₃), magnesium nitrate (Mg(NO₃)₂), sodium chloride (NaCl), ammonium sulfate ((NH₄)₂SO₄), potassium chloride (KCl), potassium nitrite (KNO₂) and potassium sulfate (K₂SO₄) were used to equilibrate the product sample with respective water activity. The salts were dissolved in distilled water at 100°C and cooled to each test temperature for crystallization to form a saturated slushes. The saturated slush level was maintained to a depth of about 0.4 cm in each sorption container. The sorption containers were allowed to equilibrate at desired temperature for four days before the product sample was placed into them. After taking the tare weight of weighing dish approximately 2 g of freshly made product sample was weighed in each container. To prevent mould growth potassium sorbate (5 mg) was added to each sample to inhibit microbial growth. The weights of the samples were recorded at regular interval (after every 72 h) and apparent equilibrium was judged to have been attained when difference between the three consecutive weights did not exceed 1 mg. The equilibrium period ranged from 3 to 4 weeks.

Sorption models

The different sorption models presented below were chosen to fit the experimental sorption data as they are most widely used for several foods.

BET :

\[ \frac{a_w}{W} (1-a_w) = 1/ W_0 K + a_w (K-1)/ W_0 K \]  
(1)

GAB :

\[ W = W_0 G K a_w / [(1 - K a_w) (1 - K a_w + G K a_w)] \]  
(2)

Caurie:

\[ \ln 1/W = -\ln 1/C W_0 + 2C/W_0 \ln [ 1 - a_w / a_0 ] \]  
(3)

Where \( a_w \) is water activity, \( W \) is equilibrium moisture content, \( W_0 \) is monolayer moisture content at percent (dry basis), ‘G’ is the Guggenheim constant and ‘K’ is a correction factor for properties of multilayer molecules with respect to the bulk liquid.

BET monolayer moisture content is sometimes considered the most stable moisture content for a product. However, as reported BET relationship is only valid up to \( a_w = 0.55 \). Caurie’s plot of \( (1 - a_w / a_0) \) vs. \( \ln 1/W \) was used to obtain Caurie’s slope ‘S’. The number of adsorbed monolayer (N) was obtained using the formula:
Density of sorbed water is represented by 'C' in Caurie's equation and the surface area of adsorption (m²/g) was determined with the following formula:

\[ A = \frac{5454}{S} \] (5)

In order to check the precision of fit of the sorption data in models tested ‘R²’ and %RMS were calculated.

\[ R^2 = \sum (x_i - x_d)^2 / (x_i - x)^2 \] (6)

\[ \% \text{RMS} = \sqrt{\frac{1}{n} \sum (x_i - x_d)^2} \times 100 \] (7)

Where, ‘n’ is the number of observations, ‘x_d’ is the experimental value, ‘x’ is the value obtained by the fitting model for the i_th observation, ‘x’ is an absolute mean.

Isosteric heat of sorption

The Clausius-Clapeyron equation relates the water activities and temperatures at fixed moisture content.

\[ q_{st} = R \left[ \frac{T_1 T_2}{T_2 - T_1} \right] \ln \frac{a_{w1}}{a_{w2}} \] (8)

Where, ‘q_{st}’ is the net isosteric heat of sorption (kJ/mol), ‘R’ is the universal gas constant (8.314 J deg⁻¹ mol⁻¹ K⁻¹) and ‘T_1, T_2’ are the absolute temperatures. Slope of plot of ln (a_{w1}) versus 1/T at constant specified moisture content gave the net isosteric heat of sorption. The isosteric heat of sorption (Q_{st}) can be calculated by adding the latent heat of vaporization of pure water (ΔH_v) to neat isosteric heat of sorption (q_{st}).

\[ Q_{st} = q_{st} + ΔH_v \] (9)

The latent heat of vaporization of pure water (ΔH_v) at 25°C (average of two temperatures, 10°C and 40°C) is 44.08 kJ mol⁻¹.

Result and Discussion

Adsorption isotherm

The adsorption isotherms of sandesh powder were measured at the temperatures of 10°C, 20°C, and 40°C between the relative humidities 0.11 - 0.97. The initial moisture content of the sandesh powder samples was 0.94g water/100g solids. The isotherms plotted by joining the experimental values of an equilibrium moisture contents (EMC) against the different water activities (a_w) at different temperatures are presented in Figure 1. Each data point indicated in the curves was the average of two experimental determinations. The curves resulted due to effects of Raoult’s law, capillary effects and surface water interactions in the product (Stencel., 1999).

The isotherms obtained are sigmoid in shape and correspond to type – II as per the classification proposed by Brunauer et al. (1940). Two bends are noted in each curve, these are the result of changes in the magnitude of the separate physical-chemical effects. Figure 1 indicates that, EMC rose gradually at lower water activities 0.12 - 0.57 at 10°C, 0.12 - 0.55 at 20°C and 0.11 – 0.51 at 40°C followed by a steep rise at higher water activities. The moisture content in sandesh powder increased from 2.66% to 24.48%, 3.29% to 48.78% and 2.87% to 45.75% when a_w increased from 0.12 to 0.97 at 10°C, 20°C and 40°C respectively.

As reported for other Indian dairy products, adsorption isotherm of sandesh powder also exhibit three regions, typical for milk proteins. Water uptake was rapid in region I, slowed down in region II and was accelerated in region III. Region II includes multiplayer water, which is under transition to natural properties of free water. Some of this water is available for chemical reactions. Water in region III is in free state held into voids, crevices and capillaries (Kinsella and Fox, 1987).

Effect of temperature on sorption isotherm

Since water sorption generally decreases with increasing temperature, in sandesh powder, equilibrium moisture content was lower at higher temperatures till the water activity reached to 0.79. A clear-cut inversion was noticed above 0.79 a_w implying increase in EMC at higher temperatures. This can be ascribed to an increase in solubility of sugars in water at higher temperatures. The intersection point depends on the composition of the food and solubility of sugars (Weisser et al.,1982). Occurrence of similar intersection was also observed in sugar rich food systems viz. resins, figs, prunes, biscuits, kheer, basundi mix, etc.

The negative temperature effect on the EMC has often been reported in foods with high protein content (Okos et al., 1992; Delgado and Sun, 2002a, b; Jayendra Kumar et al., 2005). The change in water activity due to temperature has been ascribed to changes in water binding, dissociation of water and or increase of solute solubility in water as reported by Rahman (1995). It is also reported that a higher temperature results in a greater activation of the water molecules, which then breaks away from the water binding sites thereby lowering the EMC (McMinn & Magee,2003; Sharma et al., 2009).

Isotherm models

Three isotherm models (Eqs.1–3) were attempted for testing the fitness of experimental data. For sandesh powder all three models BET, GAB and Caurie were found to bear close relationship indicated by R² and %RMS values given in Table 1-2. Models helps to predict the experimental moisture sorption data and to characterize the sorption behavior of the product. The difference in EMC at 10°C and 40°C at same moisture contents as predicted by GAB equation and plotted as a function of moisture content given in Figure 2. The Figure 2 indicates that as the moisture
content increased, effect of temperature on water activity decreased. Figure 3 shows the experimental and predicted values obtained using GAB equation for adsorption of moisture in sandesh powder at 10°C, 20°C and 40°C. Figure 3 shows satisfactory agreement between experimental and predicted values.

## Table 1 Monolayer value obtained from sorption isotherm equations for sandesh powder at different temperatures

<table>
<thead>
<tr>
<th>Equation</th>
<th>Temp. °C</th>
<th>Monolayer moisture (g water/100g dry solids)</th>
<th>R²</th>
<th>%RMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>10</td>
<td>2.98</td>
<td>0.99</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>2.23</td>
<td>0.89</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.56</td>
<td>0.99</td>
<td>1.12</td>
</tr>
<tr>
<td>GAB</td>
<td>10</td>
<td>3.3</td>
<td>0.98</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>2.3</td>
<td>0.92</td>
<td>7.51</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.42</td>
<td>0.96</td>
<td>7.10</td>
</tr>
</tbody>
</table>

## Table 2 Properties of sorbed water of sandesh powder at different temperatures

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>No. of adsorbed monolayers N</th>
<th>Density of sorbed water (g/cc)</th>
<th>Surface Area of sorption (m²/g)</th>
<th>Coefficient of Regression of Percent Root mean square R²</th>
<th>Percent Root mean square %RMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.79</td>
<td>1.99</td>
<td>103.49</td>
<td>0.98</td>
<td>27.99</td>
</tr>
<tr>
<td>20</td>
<td>3.40</td>
<td>2.20</td>
<td>92.69</td>
<td>0.95</td>
<td>28.46</td>
</tr>
<tr>
<td>40</td>
<td>2.73</td>
<td>2.87</td>
<td>74.38</td>
<td>0.97</td>
<td>33.96</td>
</tr>
</tbody>
</table>

## Table 3 Equilibrium water activity of sandesh powder at different moisture contents

<table>
<thead>
<tr>
<th>Moisture content (g/100g dry solids)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>0.16</td>
</tr>
<tr>
<td>4</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>0.41</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>0.57</td>
</tr>
<tr>
<td>8</td>
<td>0.63</td>
</tr>
<tr>
<td>9</td>
<td>0.67</td>
</tr>
<tr>
<td>10</td>
<td>0.71</td>
</tr>
<tr>
<td>11</td>
<td>0.74</td>
</tr>
<tr>
<td>12</td>
<td>0.77</td>
</tr>
<tr>
<td>14</td>
<td>0.80</td>
</tr>
<tr>
<td>15</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Properties of sorbed water

Properties of sorbed water in sandesh powder were determined at 10°C, 20°C and 40°C. The value of monolayer moisture content at each temperature was calculated using BET and GAB equation and presented in Table 1. Generally monolayer moisture content decrease with an increase in temperature (Iglesias & Chirife, 1976a,b). In sandesh powder BET monolayer value decreased from 2.98g of water/100 g of solids at 10°C to 2.23g of water/100 g of solids at 20°C followed by further decrease to 1.56g of water/100 g of solids at 40°C. GAB monolayer value gradually decreased from 3.30g of water/100 g of solids at 10°C to 2.30g of water/100 g of solids at 20°C followed by decline to 1.42g of water/100 g of solids at 40°C.

Though the BET model is valid over the limited range of water activity, the BET monolayer value in sandesh powder represents tightly bound water and could be suggested as optimum water content for the stability of milk products. The chemical reactions depending on salvation are therefore expected to be slow in monolayer region of sandesh powder. Properties of sorbed water as calculated from Caurie equation for sandesh powder is presented in Table 2. Number of adsorbed monolayers decreased from 3.79 at 10°C to 3.40 at 20°C, followed by further gradual decline to 2.73 at 40°C. Density of sorbed water increased with an increase in temperature from 10°C to 40°C. Similar trends were also been observed in basundi mix powder by Sharma et al., (2009). Surface area of sorption decreased from 103.49m²/g to 74.38m²/g when temperature increased from 10°C to 40°C. This indicates that the total number of binding sites decreased due to protein-protein, protein–carbohydrate and protein- lipid
Figure 1 Sorption isotherms of sandesh powder at different temperatures

Figure 2 Difference in EMC in sandesh powder at 10°C and 40°C at the same moisture content plotted as a function of moisture content
Figure 3 Predicted values of the equilibrium moisture content in sandesh powder at 10°C, 20°C and 40°C using GAB model

Figure 4 Sorption isosters of sandesh powder at different moisture contents

Figure 5 Isosteric heat of sorption of sandesh powder with moisture contents
interaction in sandesh powder. This also clearly indicates a reduction in exposure of charged polar groups and carboxyl function of peptide bonds that binds water in the product as reported by Jayendra Kumar et al., (2005).

Heat of sorption

The equilibrium water activity in sandesh powder at different moisture content (3-15 g/100g solids) were calculated by interpolation of the experimental data obtained from GAB equation and given in Table 3. The increase in water activity with temperature at constant moisture content indicates that the sorption in sandesh powder was an exothermic process, making the product more susceptible to microbial spoilage (Labuza et al., 1985; Bolin, 1980). Figure 4 shows sorption isotherms of sandesh powder at different moisture content (3-10g/100g dry solids). The sorption isotherms did not show temperature dependence over a temperature range of 10-40°C. Therefore, the net isosteric heat of sorption values were calculated by employing Clausius-Clapeyron equation (Eqn. 8) by considering 10°C and 40°C as T1 and T2. The curve plotted (Figure 5) at the mean temperature (10°C and 40°C) as 25°C. The heat of desorption decreased with corresponding increase in moisture content, initially rapidly up to 12 g of water/100 g of solids and later approached a constant value. Similar trends were also observed in many other traditional Indian dairy products (Sharma et al., 2009; Jayendra Kumar et al., 2005; Sawnhney et al., 1991). The decrease in the net isosteric heat of sorption in sandesh powder with increase in amount of water sorbed is due to availability of most active sites, leads to higher energy of interaction between the sorbate and the sorption sites. As these active sites become unavailable, sorption subsequently occurred on less active sites giving lower heat of sorption (Iglesias & Chirife, 1976b,c; Delgado & Sun, 2002b; Jayendra Kumar et al. and 2005; Rao et al., 2006). The isosteric heat (67.5,60.25,54.64,51.64,49.48,47.70,46.85,46.07,45.37and 44.71kJmol−1 at 2,4.3,6.5,6.7,8,9, 10, 11 & 12 g moisture/100g dry solids, respectively) had strong dependence on moisture content as energy required increased greatly at low equilibrium moisture content. Similar observations were reported for many other traditional Indian dairy products (Sharma et al., 2009; Rao et al., 2006; Jayendra Kumar et al., 2005)

Conclusions

Moisture adsorption isotherms of sandesh powder were studied in the temperature range of 10-40°C. The sorption isotherms curves obtained were sigmoid in shape and classified as type II. The sorption isotherms in sandesh powder exhibit negative temperature effect as EMC was higher at lower temperature for a similar water activity. A Clear-cut inversion was observed above the aω of 0.75 thereby indicating higher EMC at a higher temperature of sorption which is the characteristics of sugar-rich foods. Sorption data borne out the best fit with BET, GAB and Caurie model. Monolayer moisture obtained from both BET and GAB models decreased with an increase in temperature. Properties of sorbed water were estimated to understand the behavior of sorbed water due to change in temperature. The net isosteric heat of sorption values derived from GAB parameters indicated that the energy requirement for the drying process would increase considerably below 12% moisture content. The information generated would be useful to understand drying, packaging conditions and to develop long life, ready to eat, ready-to-serve product. The study may further be extended to develop shelf life prediction models for sandesh.

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