Storage Stability of *Sandesh* – an Indian Milk Sweet

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ABSTRACT

Storage stability of *sandesh*, one of the popular Indian milk sweets was determined in terms of its moisture adsorption isotherms by gravimetrically at 20 and 30°C using saturated salt solutions in the range of 11.2 and 97.2%. The isotherms obtained were of sigmoid shape and of the BET type. Out of three sorption models fitted to the experimental data, Caurie model was found superior in interpreting the moisture adsorption characteristics of *sandesh* with low relative deviation percent and high coefficient of determination. The values of isosteric heat of sorption as calculated from Clausius–Clapeyron equation was found to increase with decreasing moisture content at lower moisture content and approached the value of heat of vaporization of free water above 17.25% (db).

**Keywords:** *Sandesh*, Indian milk sweets, moisture sorption isotherm, isosteric heat of sorption, Clausis-Clapeyron equation, GAB model, BET model, and Caurie model.

1. INTRODUCTION

*Sandesh* is one of the heat-acid coagulated products in India. It is popular due to its palatability and aroma. It is a rich source of milk protein, fat, carbohydrate and the vitamins like *A* and *D*. Chhana, a heat-acid coagulated product of milk forms the base material for the preparation of *sandesh*. In the preparation of *sandesh*, milk is heated to 90-95°C, followed by cooling to 70°C. A coagulating solution such as citric acid, calcium lactate, lemon juice or sour whey, previously heated to 70°C is added to the heated milk to precipitate the milk. The precipitation of milk involves the formation of large structural aggregates of whey protein such as α-lactalbumin (α-la), β-lactoglobulin (β-la), bovine serum albumin (BSA), immunoglobulins (Ig), and polypeptides proteose peptones (PP), in which milk fat, other colloidal and soluble solids such as carbohydrate, calcium, phosphate, vitamins (thiamine, riboflavin, niacin, ascorbic acid, vitamin *B*₁₂, folic acid etc.), nitrogenous materials (ammonia, amino acid, urea, creatine etc.), entrained with whey. The whey is drained out by using muslin cloth. The dewheyed product, called chhana, is kneaded into a uniform dough,
mixed with sugar and cooked over low flame with constant scraping until the mixture gets the desired consistency and flavor (Aneja et al. 2002). The cooked chhana-sugar mixture is allowed to cool and set at room temperature. The product is then shaped by using moulds of various shapes. Moisture content of sandesh generally varies between 12-14% (wb) (Rajorhia and Sen, 1985). Sandesh by virtue of its lower moisture and higher sugar content is expected to be less susceptible to microbial spoilage. However, prolonged storage under ambient condition adversely affects consumers’ acceptability due to microbial changes in the flavor profile such as taste, smell, texture and color.

Despite availability of a variety of water-based criteria, which can give an indication of the stability of food, water activity is the most effective and useful measurement of water in food. Sorption isotherms describe the equilibrium relationship between water activity and moisture content of a food at constant temperature. Moisture sorption isotherms give an insight into the moisture-binding characteristic of a food. Hence, knowledge of the moisture sorption characteristic of a food is important for prediction of its quality, stability and shelf-life during its packaging and storage (Vilades et al., 1995).

Moisture sorption characteristics of various foods have been reviewed by Boquet et al., (1978), Chirif and Iglesias (1978) and van den Berg and Bruin (1981). Moisture sorption isotherms of various milk products including Peda (Biradar et al., 1985), Chhana powder and Casein (Bandyopadhyay et al., 1987), Khoa (Sawhney and Cheryan 1988), Dudh churpi (Hossain et al., 2002), Chhana poda (Rao et al., 2006), Milk powder and Milk products (Berlin 1981a; Berlin et al., 1968a; Berlin et al., 1968b; Jouppila and Roos 1994; Lomauro et al., 1985; Stencel 1999), Mango-soy-fortified yogurt powder (Kumar and Mishra 2006) have already been reported. However, studies on water sorption isotherms of sandesh have not been reported in order to predict its proper storage conditions and packaging systems.

The value of monolayer moisture content of a food gives an indication of total number of polar groups binding water and the level of hydration, at which the mobility of small molecules become apparent. The importance of knowing the water activity at which the monolayer exists is that it appears to be the most stable water content for food in relation to its shelf-life, because foods prepared to and maintained at moisture content just above the monolayer value would presumably be chemically more stable than any other moisture content. Moisture sorption is influenced by the surface area and number of surface binding sites i.e., physical stability like porosity and microstructure, the influence of temperature on monolayer moisture content, number of absorbed monolayers, density of sorbed water, surface area of adsorbent and per cent bound water are required to be studied.

Isosteric heat of sorption often referred to as differential heat of sorption is used as an indicator of binding energy of absorbed water by solid particles (Fasina et al., 1997). Estimation of the isosteric heat of sorption data from isotherms at two or more temperatures by using Clausius-Clapeyron type equations allows prediction of isotherms at any conditions.
temperature. The present paper describes the moisture adsorption characteristic of sandesh at 20 and 30°C to evaluate the applicability of various existing sorption models for their ability to fit the adsorption data and to calculate the properties of sorbed water.

2. MATERIALS AND METHODS

2.1 Sample Preparation

Standardized cow milk of 4% fat and 8.5% SNF was used for the preparation of chhana. Citric acid solution was used as the coagulating agent. The strength of the acid solution \( b \) required for the milk coagulation was calculated from the following equation (Jonkman and Das, 1993).

\[
X_{ma} = \frac{C_m w_m + b \left( \frac{M_{la}}{M_{ca}} \right) w_{ca}}{w_m + w_{ca}}
\]

where, \( X_{ma} \) is the acidity of milk-acid mixture at the time of coagulation (% lactic acid), \( C_m \) is the acidity of fresh milk (% lactic acid), \( w_m \) is the weight of fresh milk (kg), \( b \) is the strength of citric acid solution (%), \( M_{la} \) is the molecular weight of lactic acid (90 g.mol\(^{-1}\)), \( M_{ca} \) is the equivalent weight of citric acid (64 g.mol\(^{-1}\)) and \( w_{ca} \) is the weight of citric acid solution (kg). The ratio of weight of milk to citric acid solution was maintained at 5:1 (Choudhary et al., 1998). The acidity of milk-acid mixture at the time of coagulation was maintained at 0.52% lactic acid (Choudhary et al., 1998). Substituting the values of \( X_{ma}=0.52, C_m=0.165, w_m=1, M_{la}=90, M_{ca}=64, w_{ca}=0.2 \) into Eqn. (1), the strength of the citric acid solution was found to be 1.62%.

For the coagulation of milk, a continuous chhana-making unit of capacity 60 litre milk per hr was used (Sahu et al., 2006). In the unit, milk was heated to 95±2°C and citric acid solution of 1.62% strength at 17°C temperature was injected to the heated milk. The moisture content of the chhana obtained from the continuous chhana-making unit was 0.602 kg per kg chhana. In order to reduce the moisture content of the chhana to 0.48 kg per kg chhana (Kumar, 1998), the chhana was centrifuged by using a double wall basket centrifuge (Pastuer Engg. Pvt. Ltd., Co., Kolkata, India) for 10.74 min at 1200 rev.min\(^{-1}\). 4.5 kg of the centrifuged chhana kneaded into a uniform dough in a jacketed scraped surface agitated vessel for 4.5 min (Sahu 2007). Cane sugar at the rate of 30% of the weight of chhana was mixed to it. The chhana and sugar was mixed and cooked in the vessel at rotor speed of 70 rev.min\(^{-1}\) for 15 min at an absolute steam pressure of 2 kg.cm\(^{-2}\) (Sahu, 2007). The cooked chhana-sugar mixture was allowed to cool at room temperature and shaped by using a single screw vertical extruded attached with an electro-mechanical cutting (Pastuer Engg. Co., Pvt. Ltd, Kolkata, India).

2.2 Determination of Equilibrium Moisture Content

The standard gravimetric method was adopted to obtain adsorption isotherm of sandesh (van den Berg and Bruin, 1981; van dern Berg, 1984; Tsami et al., 1990; Sen, 1987; Kumar, 1998; Kumar and Mishra, 2006; Jena, 2006). Saturated salt solutions giving a range of relative humidity as mentioned in Table 1 at 20 and 30°C were prepared. Each solution was transferred to airtight glass desiccators. Duplicate samples (5 to 10 g) of sandesh were weighed in small petri dishes and placed above the saturated salt solutions inside the desiccators, which were tightly closed. Before placing the samples, potassium sorbate at 0.5% by weight was spreaded over the samples to prevent mould growth during the storage.

The desiccators containing the samples were placed in an incubator maintained at a particular temperature for equilibration. The samples in the desiccators were weighed periodically until constant weighing was obtained. The total time for removal, weighing and replacing the samples was less than 10s. This minimized atmospheric moisture sorption during weighing. Equilibrium was considered to have reached when the difference between two successive weighings was less than 1 mg. The moisture content of the sample was measured by the vacuum oven method at 70°C and 100mm Hg pressure for 48 hr.

Table 1. Relative humidity of saturated salt solutions at 20°C and 30°C

<table>
<thead>
<tr>
<th>Salt</th>
<th>Relative humidity (RH), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>Lithium chloride</td>
<td>11.4</td>
</tr>
<tr>
<td>Potassium acetate</td>
<td>23.1</td>
</tr>
<tr>
<td>Magnesium chloride</td>
<td>33.1</td>
</tr>
<tr>
<td>Potassium carbonate</td>
<td>43.2</td>
</tr>
<tr>
<td>Magnesium nitrate</td>
<td>54.1</td>
</tr>
<tr>
<td>Potassium iodide</td>
<td>69.9</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>75.5</td>
</tr>
<tr>
<td>Ammonium sulphate</td>
<td>81.3</td>
</tr>
<tr>
<td>Potassium sulphate</td>
<td>97.2</td>
</tr>
</tbody>
</table>

3. MODELING OF ADSORPTION ISOTHERMS

3.1 Fitting Moisture Sorption Models

The adsorption data obtained at 20°C and 30°C for sandesh samples were fitted into three sorption models viz., Brunauer-Emmett-Teller (BET), Caurie and Guggenheim-Anderson-de Boer (GAB). These models are given in Table 2. The experimental data were fitted to these models and the respective model constants were found out using SYSTAT 8.0 software. Experimental data for water activity values less than 0.5 were used to fit the BET model as

this model is known to be valid below this value of water activity (Chirife and Iglesias, 1978; van den Berg and Bruin, 1981; van dern Berg, 1984; Tsami et al., 1990; Sen, 1987; Kumar, 1998; Kumar and Mishra, 2006; Jena, 2006).

The adequacy of the developed relationship between predicted and experimental values of equilibrium moisture content was estimated in terms of standard error of estimate (SE) on EMC and relative deviation percent (Rd) as follows.

\[
SE = \sqrt{\frac{\sum (M_{ai} - M_{pi})^2}{F}}
\]

\[
R_d = \frac{100}{N} \sum \frac{|M_{ai} - M_{pi}|}{M_{ai}}
\]

where, \(M_{ai}\) and \(M_{pi}\) are respectively the actual and predicted values of equilibrium moisture content, \(N\) is the number of observations and \(F\) is the degree of freedom of the regression model. In general, it is considered that the relative deviation percent, \(R_d\) below 10% gives a very good fit.

Table 2. Moisture sorption isotherm models fitted to the experimental data

<table>
<thead>
<tr>
<th>Models</th>
<th>Equations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>(\frac{a_w}{(1-a_w)M} = \frac{1}{M_m C_b} + \frac{(C_b-1)M_m C_b}{M M_m C_b-a_w})</td>
<td>Chirife and Iglesias (1978); Brunauer et al. (1938)</td>
</tr>
<tr>
<td>Caurie</td>
<td>(\frac{1}{M} = \frac{1}{M_m C_c} \left( \frac{(1-a_w)}{a_w} \right)^{2C_c} )</td>
<td>Caurie (1981)</td>
</tr>
<tr>
<td>GAB</td>
<td>(\frac{M}{M_m} = \frac{C_g k_j a_w}{(1-k_j a_w)(1-k_j a_w-C_g k_j a_w)})</td>
<td>Bizot (1983); van den Berg (1984); Rizvi (1995); Tsami et al. (1990); Sopade and Ajisegiri (1994)</td>
</tr>
</tbody>
</table>

where, \(a_w\) = water activity (fraction), \(M_e\) = equilibrium moisture content (kg.kg dry solid\(^{-1}\)), \(M_m\) = monolayer moisture content (kg.kg dry solid\(^{-1}\)), \(C_b\) = BET constant, \(C_c\) = Caurie’s constant, and \(C_g\) and \(k_g\) = GAB constants.

3.2 Properties of Sorbed Water

The number of absorbed monolayers \(N\) was calculated using following formula (Caurie, 1981).

\[
N = \frac{M_m}{C_c}
\]
where, $M_m$ (kg.kg dry solid\(^{-1}\)) is the monolayer moisture content as calculated from Caurie’s model and $C_c$ (g.cm\(^{-1}\)) is Caurie’s constant. The percent bound water was expressed as $M_m^*N$. Assuming that the magnitude of $C_c$ in the Caurie’s model is equivalent to the density of absorbed water in the monolayer, the surface area of absorbent $A$ was calculated as:

$$A = \frac{M_m}{C_c \times d \times 10^8}$$  \hspace{1cm} (5)

where, $d$ is the diameter of water molecule i.e. $3.673 \times 10^{-10}$ m.

### 3.3 Net Isosteric Heat of Sorption

Net isosteric heat of sorption provides an estimation of the heat required to be removed in excess of latent heat of vaporization of pure water, for extracting absorbed water at a particular moisture content. Since, the sorption data are obtained at different temperatures, it is possible to evaluate the net heat of sorption $q_{st}$ (kJ.kg water\(^{-1}\)) at various moisture contents using the best-fit isotherm. The value of $q_{st}$ (kJ.kg water\(^{-1}\)) can be computed by using the Clausius–Clapeyron equation (Labuza et al., 1985);

$$\ln \left(\frac{a_{w2}}{a_{w1}}\right) = \frac{q_{st}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$  \hspace{1cm} (6)

where, $a_{w1}$ and $a_{w2}$ are the water activities (decimal) at temperatures $T_1 \,(20+273=293K)$ and $T_2 \,(30+273=303K)$ respectively. $q_{st}$ (kJ.kg\(^{-1}\)) is the net isosteric heat of sorption, and $R$ is the universal gas constant (8.314 kJ.mol\(^{-1}\).K\(^{-1}\)).

Isosteric heat of sorption $Q_{st}$ (kJ.kg\(^{-1}\)) was calculated from the following relationship;

$$Q_{st} = q_{st} + \Delta H_v$$  \hspace{1cm} (7)

where, $\Delta H_v$ (kJ.kg\(^{-1}\)) is the latent heat of vaporization of pure water at the mean value of two temperatures i.e., (20+30)*0.5 i.e., 25°C used in the study. The value of $\Delta H_v$ at 25°C was taken as 2442.50 kJ.kg\(^{-1}\).

### 4. RESULTS AND DISCUSSION

#### 4.1 Sorption Isotherm of Sandesh

The initial moisture content of the sandesh samples was 15.10±0.853% (db). The sorption isotherms of the samples at 20°C and 30°C are presented in Fig. 1. The figure shows the relationship between $a_w$ and EMC data is smooth and sigmoid shaped at both the temperatures. On the isotherms, three zones are noted; zone-I ($a_w$: 0.0–0.2), zone-II ($a_w$: 0.2–
0.6) and zone-III ($a_w$: 0.6–1.0). The moisture uptake was slow in the zone-I followed by a linear and slow and steady rise in the zone-II and a subsequent accelerated rise in the zone-III. In sandesh apart from sugar, the product contains casein, precipitated during the acid-heat coagulation of milk. Since proteins are the preferred sorption sites at low water activities, the sorption in the low water activity range is presumably due to casein era. The steep acceleration of sorption at high water activities could be due to the solubilization of sugar. That is, the crystallization of sucrose and beta-lactose present in sandesh have a fairly low adsorption of water until water activity becomes sufficient for solubilization and subsequent adsorption increases as observed in Chhana poda (Rao et al., 2006).

![Fig. 1. Moisture adsorption isotherm of sandesh at 20°C and 30°C](image)

**Table 3.** Computed values of constants of isotherm models fitted to sorption data of sandesh

<table>
<thead>
<tr>
<th>Isotherm Models</th>
<th>Temperature ($^\circ$C)</th>
<th>Model constants</th>
<th>$R^2$</th>
<th>$R_d$</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BET</strong></td>
<td>20</td>
<td>$C_b = 12.67$</td>
<td>$M_m = 5.714$</td>
<td>0.955</td>
<td>9.245</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$C_b = 9.056$</td>
<td>$M_m = 5.121$</td>
<td>0.988</td>
<td>8.253</td>
</tr>
<tr>
<td><strong>Caurie</strong></td>
<td>20</td>
<td>$C_c = 2.304$</td>
<td>$M_m = 5.892$</td>
<td>0.992</td>
<td>9.247</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$C_c = 1.910$</td>
<td>$M_m = 5.235$</td>
<td>0.989</td>
<td>8.242</td>
</tr>
<tr>
<td><strong>GAB</strong></td>
<td>20</td>
<td>$C_g = 9.268$</td>
<td>$M_m = 5.258$</td>
<td>0.958</td>
<td>10.248</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$C_g = 6.259$</td>
<td>$M_m = 4.854$</td>
<td>1.362</td>
<td>1.189</td>
</tr>
</tbody>
</table>

A rise in temperature causes an increase in water activity at the same moisture content. At high temperature, kinetic energy of water molecules is high and water adsorption is low. This indicates that the material becomes less hygroscopic at higher temperatures. These effects are prominent especially up to 0.6 water activity. At higher temperature the kinetic energy of the water molecules was high and water absorbance at a given water activity was low (Demertzis et al., 1989). Sandesh is a rich source of protein and carbohydrate. Since protein and carbohydrate are known to have high water binding capacity at low temperature than at

higher temperature, the observed reduction in water binding capacity at 30°C as compared to 20°C could be attributed to the high protein and carbohydrate content of *sandesh*. The effect of temperature on equilibrium moisture contents of *sandesh* was found significant from the analysis of variance (ANOVA) of the experimental data (probability $p > 0.05$). Berlin *et al.*, (1973) reported reduction in moisture sorption by whey proteins when the temperature was increased from 24 to 35°C. Rao *et al.*, (2006) observed the similar effect in Chhana poda – an Indian baked milk sweet.

### 4.2 Modeling of Sorption Isotherms

Table 3 shows the values of model constants fitted to the experimental data along with their $R^2$, $R_d$, and $SE$ values. Of three models fitted to the data, Caurie model was found good to predict the data as exhibited by higher $R^2$ and lower $R_d$ value. Fig. 2 shows the predicted values of equilibrium moisture content for *sandesh* with the best-fitted Caurie’s model at 20°C and 30°C. The Caurie’s model has been fitted successfully to characterize the sorption characteristic of Dudh churpi (Hossain *et al.*, 2002) and Milk powder, Casein, Skim milk and Lactose (Bandyopadhyay *et al.*, 1987). At high temperature BET model gave an adequate fit to the adsorption data of *sandesh*. At both the temperatures, GAB model did not show any relevant fit to the adsorption data of *sandesh* due to low $R^2$ and high $R_d$ value.

### 4.3 Properties of Sorbed Water

Table 4 represents the values of density of sorbed water, number of absorbed monolayers, per cent bound water and surface area of absorbent as calculated from Caurie model at 20°C and 30°C. The data show that the values of density of sorbed water, number of absorbed monolayers, percent bound water and surface area of absorbent decreases with the increase in temperature of sorption from 20 to 30°C. The monolayer moisture content from Caurie’s model for 20°C and 30°C were 5.892 and 5.205% respectively. The estimated BET monolayer values (Table 4) were in good agreement with the value of 5.5% reported for Casein (Kinsella and Fox 1987) and 5.565 and 4.834% at 5°C and 35°C respectively for Chhana poda (Rao *et al.*, 2006). Biradar *et al.*, (1985) reported the monolayer for Peda as calculated from BET model as 8.73%. Bandyopadhyay *et al.*, (1987) determined the monolayer moisture contents of Casein, Lactose and Chhana powder from BET equation as 4.9, 2.2 and 1.9% respectively. The same author reported the Caurie’s monolayer values as 6.3, 4.0 and 5.2% for the respective milk products. Biradar *et al.*, (1985) also reported the monolayer value for Peda as calculated by BET model as 8.73% (*db*).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$M_m$ (%)</th>
<th>$C_c$ (g.cm$^{-2}$)</th>
<th>$N$</th>
<th>Bound water (%)</th>
<th>$A$ (m$^2$.g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.892</td>
<td>2.204</td>
<td>2.673</td>
<td>15.749</td>
<td>72.774</td>
</tr>
<tr>
<td>30</td>
<td>5.205</td>
<td>1.999</td>
<td>2.604</td>
<td>13.726</td>
<td>70.890</td>
</tr>
</tbody>
</table>

4.4 Isosteric Heat of Sorption

The evaluation of isosteric heat of sorption $q_{st}$ as a function of equilibrium moisture content at average temperature of 25°C (i.e. 0.5*(20+30)) was carried out by using Eqn. (6) to the adsorption data at 20°C and 30°C by using the best-fit Caurie model. Fig. 3 represents the variation of isosteric heat of sorption with equilibrium moisture contents. The figure shows that the isosteric heat of sorption decreased as the moisture content increased and remained constant above 17.25% ($db$). This could be explained quantitatively considering that, initially the adsorption occurs on the most active sites involving high interaction energies. As these active sites become occupied, adsorption subsequently occurs on the less active sites involving lower interaction energies. Large values of $Q_{st}$ at low moisture content indicate stronger interactions between water vapor and sandesh. This type of behavior has been observed by Sawhney et al., (1991) in Khoa and Rao et al., (2006) in Chhana poda.
5. CONCLUSIONS

Moisture sorption characteristics of sandesh could be predicted agreeably with Caurie model. A reduction in moisture adsorption and water binding capacity was observed as the temperature of adsorption increased from 20 and 30°C. Monolayer moisture content of sandesh was found to be 5.892 and 5.235% (db) at 20 and 30°C respectively. Isosteric heat of sorption of sandesh was found to increase with decreasing moisture content suggesting endothermic reaction at lower moisture content and at higher moisture contents it approached the value of heat of vaporization of free water.

6. REFERENCES


