MOISTURE SORPTION CHARACTERISTICS OF TRADITIONAL INDIAN DAIRY PRODUCT "THABDI"

THESIS SUBMITTED TO THE
NATIONAL DAIRY RESEARCH INSTITUTE, KARNAL
(DEEMED UNIVERSITY)
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE

MASTER OF TECHNOLOGY
IN
DAIRY ENGINEERING

BY

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B.Tech (DT)

DAIRY ENGINEERING DIVISION
NATIONAL DAIRY RESEARCH INSTITUTE
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KARNAL-132001 (HARYANA), INDIA

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Approved by:

24.7.13
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CERTIFICATE

This is to certify that the thesis entitled **"MOISTURE SORPTION CHARACTERISTICS OF TRADITIONAL INDIAN DAIRY PRODUCT "*THABDI*"** submitted by **Ms. Vankar Kesha Dinesh** towards the partial fulfilment of the requirements for the award of the degree of **Master of Technology in Dairy Engineering** of the **National Dairy Research Institute (Deemed University)**, Karnal (Haryana), India, is a bonafide research work carried out by her under my supervision and guidance and no part of the thesis has been submitted for any other degree or diploma.

Dated: 26th July, 2013

Dr. I. K. SAWHNEY
MAJOR ADVISOR & CHAIRMAN
(GUIDE)

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Dated: July, 2013 *Kesha. D. Vankar*

Dedicated to…

My beloved parents

and

My guide

Dr. I. K. Sawhney

ABSTRACT

Traditional Indian dairy products and sweets have large consumer base. These products are an integral part of Indian culture and have great social, religious, cultural, medicinal and economic importance. *Thabdi* is one such region specific milk sweet manufactured traditionally in Saurashtra region of Gujarat State. Water activity is considered as one of the most important parameter in food preservation and processing. Understanding and control of a_w contributes to safer food storage conditions and forms the basis of modern food formulation, especially for intermediate moisture foods. The overall objective of this study was to obtain sorption parameters of *thabdi* prepared from buffalo milk at different temperature and to find out the temperature dependence of parameter of best fitted equation. Moisture sorption characteristics of *thabdi* prepared from buffalo whole milk at 15, 25 and 35ºC were determined using a gravimetric-static method. Sorption isotherm followed a type II (sigmoid) shape. Equilibrium moisture content decreased with increase in temperature at constant water activity. GAB, Modified Mizrahi, Oswin, Caurie and Halsey models were applied to the isotherm data. The GAB model, which was having least RMS% value, selected as best fitted equation. Temperature dependence of GAB parameters were determined by using Arrhenius type equation. Initial water activity of *thabdi* was 0.829 at 25ºC. Net isosteric heat was determined from sorption data using the Clausius-Clapeyron equation. The heat of sorption was found to increase initially and attain a peak value of 58.11kJ/mol at 5% moisture level and then decreased. The difference between equilibrium moisture content of *thabdi* in adsorption and desorption was found to be significant. The hysteresis energy reduced from 48.75 kJ/kg of water at 15ºC to 31.43 kJ/kg of water at 35ºC. The monolayer moisture content of *thabdi* also decreased with increase in temperature.

पारंपरिक भारतीय डेयरी उत्पाद " थाबडी " की नमी सॉर्बेशन खासियत

सारांश

पारंपरिक भारतीय डेयरी उत्पादों और मिठाई बड़े उपभोक्ता का आधार है. इन उत्पादों का भारतीय संस्कृति में एक अभिन्न हिस्सा हैं और महान सामाजिक, धार्मिक, सांस्कृतिक, औषधीय और आर्थिक महत्व है| थाबडी ऐसे ही एक क्षेत्र विशेष मिठाई गुजरात राज्य के सौराष्ट्र क्षेत्र में पारंपरिक रूप से निर्मित है| पानी गतिविधि का नियंत्रण और उसका ज्ञान खाद्य भंडारण की स्थिति के लिए योगदान देता है और विशेष रूप से मध्यवर्ती नमी खाद्य पदार्थों के लिए, आधुनिक भोजन तैयार करने का आधार बनाता है| इस अध्ययन के समग्र उद्देश्य के लिए विभिन्न तापमान पर भैंस के दूध से तैयार थाबडी की सॉर्बेशन पैरामीटर प्राप्त करने के लिए और सबसे अच्छा फिट समीकरण के पैरामीटर के तापमान निर्भरता पता लगाने के लिए किया गया था| भैंस के दूध से बने थाबडी को गुरुत्वीय स्थैतिक विधि का उपयोग करके नमी सॉर्बेशन विशेषताओं को १५, २५ और ३५ डिग्री तापमान पर प्राप्त किये गये. नमी सॉर्बेशन इसोथेर्म आकृति प्रकार द्वितीय (अवग्रह) जैसा दीखता है| लगातार पानी गतिविधि पर संतुलन नमी सामग्री में तापमान वृद्धि के साथ कमी पाई गयी| गएब, संशोधित मिजराही, कौरी, ओस्विन और हल्से मॉडल सॉर्बेशन डेटा पर लागू किये गए| गएब मॉडल, जो कम से कम आरएमएस प्रतिशत दे रहा था उसी वजयसे सबसे अच्छा फिट समीकरण के रूप में चयनित किया गया| गएब पैरामीटर के तापमान निर्भरता आर्हेनियस प्रकार के समीकरण का उपयोग करके निर्धारित किये गए थे| थाबडी की प्रारंभिक पानी गतिविधि २५ डिग्री तापमान पर ०.८२९ पाई गयी| सॉर्बेशन डेटा की नेट ऐसोस्टेरिक गर्मी क्लासुसिउस-क्लाप्रोन समीकरण का उपयोग कर से निर्धारित क़िए गए| सॉर्बेशन की गर्मी शुरू में बढ़कर ५ प्रतिशत नमी के स्तर पर ५८.११ की जुल प्रति मोल की एक शिखर मूल्य प्राप्त करने के बाद नमी के वृधि के साथ कम होती गयी| हिस्टैरिसीस ऊर्जा ४८.७५ किलो जुल प्रति किलो पानी १५ डिग्री तापमान पर पाई गयी और ३५ डिग्री तापमान पर ३१.४३ किलो जुल प्रति किलो पानी तक कम हो गयी|

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LIST OF ABBREVIATIONS AND SYMBOLS

a_w	: Water Activity
ANOVA	: Analysis Of Variance
AOAC	: Association of official Analytical Chemists
ATR-MIR	: Attenuated Reflectance Mid Infra Red
BIS	: Bureau of Indian Standards
COST	: Co-operation in the field of Scientific and Technical Research
^{o}C	: Degree Celsius
d.b.	: Dry Basis
EMC	: Equilibrium Moisture Content
et al	: et alibi, and others
g	: Gram
GAB	: Guggnheim-Andrson-De-Boer
GMP	: Good Manufacturing Practices
kg	: Kilogram
kJ	: Kilo Joules
mg	: Milligram
ml	: Milliliter
N	: Newton

%	: Percentage
R	: Gas constant (8.314 J/ degree /mol)
RMS	: Root Mean Square
SNF	: Solid Not Fat
T	: Absolute temperature (degree Kelvin)

CHAPTER – 1

Introduction

1.0 INTRODUCTION

Thabdi is a heat desiccated whole milk product sweetened with added sugar at the time of manufacture. It has brown to dark brown colour with caramelized taste and flavour. It has a distinct granular texture which is held together loosely.

Water plays critical role in food processing. Status of water in food product is a critical factor in determining safety and quality of foods. Simplest way of expressing such status is by the concept of water activity. It is generally accepted that the water activity is more closely related to microbial, chemical and physical properties of food and other natural products than is total moisture content. It predicts stability with respect to physical properties, rates of deteriorative reactions, and microbial growth. Water activity is considered as a important parameter in food preservation and processing, hence several food preservation techniques depends upon lowering water activity for reduction of the rate of microbial growth and chemical reactions

Water activity has thus become one of the most important intrinsic properties used for predicting the survival and growth of microorganisms in food due to its direct influence on product stability and quality (Scott, 1957). FDA has included the concept of water activity in its good manufacturing practices (GMP) (Labuza, 1980). Hence, minimal water activity level for growth has emerged as one of the most investigated parameters for determining water relations of microorganisms in food. Understanding and control of water activity contributes to safer food storage conditions forming basis of food formulation, especially the intermediate moisture foods.

Moisture sorption isotherm is a relationship between the equilibrium moisture content of food product and water activity at a given temperature. Such relationships help food scientist and technologist to understand water sorption properties of food, particularly when there is a need for selection of suitable packaging material and predicting stability and moisture changes during storage and even ingredient selection.

Knowledge of moisture sorption models of a given product is useful in modeling drying processes. The monolayer moisture content of a food product is an effective method of estimating the amount of bound water to specific polar sites in dehydrated food system and at this moisture the product seemed to be stable against microbial deterioration (Rahman and Labuza, 1999).

Enthalpy of adsorption and desorption is determined from isotherms at two neighboring temperatures using the Clauses-Clapeyron equation. 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). This gives an indication of binding strength of water molecules to the solids and has a bearing on energy balance of drying and freezing equation. Even the end point of drying process is determined by the desired water activity of the finished product.

For mixing operations and food formulations, isotherm of each component must be known in order to predict undesirable transfer of water from one ingredient to another, resulting in rapid deterioration of final product. Packaging is a important field of practical use of sorption isotherms (Heiss, 1968). The slope of isotherm, initial and maximum allowable water content and water activities must be known, besides the surface area and permeability of packaging material for optimizing interrelationship among these variables. Temperature dependence of sorption phenomena in food provides valuable information to characterize storage and packaging problems. Value of monolayer moisture content of food gives an indication of total number of polar groups binding water and level of hydration, at which the mobility of small molecules becomes apparent. Importance of knowing water activity at which monolayer moisture exists is that it appears to be the most stable water content for food with respect to its shelf life.

Information on moisture sorption isotherms of various traditional dairy products including khoa, burfi with sugar substitute, peda, gulabjamun mix powder, dried whey protein concentrate, ready to serve basundi mix and channa podo are available. However, the moisture sorption properties of traditional Indian dairy product “thabdi” have not been characterized so far. Keeping in view the importance and utility of moisture sorption characteristics, present study has been planned to determine these characteristics of traditional Indian dairy product "*thabdi*" prepared from buffalo milk.

Objectives of the investigation were:

I. Establishing moisture sorption isotherm of *thabdi* prepared from buffalo milk at 15, 25 & 35^{o}C.
II. Mathematical analysis of isotherm, developing equations and describing them.
III. Evaluating moisture sorption hysteresis and thermodynamics of moisture sorption isotherm.

CHAPTER – 2

Review of Literature

The given review of literature referring to processing of "*thabdi*" from buffalo milk, water activity, moisture sorption isotherm and sorption models has been described in following sub-headings:

2.1 *"Thabdi"*

2.1.1 Product description

Thabdi is a heat desiccated whole milk product sweetened with added sugar at the time of manufacture. It has brown to dark brown colour with caramelized taste and flavour. It has a distinct granular texture which is held together loosely. The product is enriched with free clarified butter fat which can be seen in form of solidified ghee on the surface as well as lightly oozing out ghee droplets throughout the mass (Patel. K., 2010). The product may be sold as loose mass or in form of rectangular pieces, the surface of which is decorated by pieces of pistachio nuts and flavoured with cardamom powder.

The variations in the compositional attributes of market sample of *"thabdi"* collected from different places are: fat:- 16.94-27.97%, protein: 11.34-16.44%, sucrose: 20.24-29.66%, lactose: 15.63-17.94%, ash: 2.21-2.97%.

2.1.2 Technology of ***"thabdi"*** processing

Krupa *et al*.,(2011), standardized the technology of manufacturing *thabdi* from buffalo milk. According to this method, buffalo milk is adjusted to Fat:SNF ratio to 0.66 and then concentrated in an open pan. After the first boiling of milk, sugar is added @8% by weight of milk. Heating is continued for 40 minutes till pat formation. The contents are held for 20 minutes for grain formation. Further the desiccation is continued till the moisture is evaporated. It is held again for 20 minutes for flavor and colour.

Open pan concentration is carried out and when first boiling is observed, sugar is added @8% by weight of milk. Concentration is continued till pre-pat formation stage is reached and then held for 20 minutes for grain development. After 20 minutes, ghee is added @1.2% to it and further desiccation is carried out for moisture evaporation. Again it is held for 20 minutes for colour and flavor development. Now big grains are clearly visible and then kettle is emptied and "thabdi" is spread in SS tray and allowed to set and get cool. It is later decorated with pistachio nuts and cardamom powder. Fig. 2.1 shows the manufacturing process flow diagram of thabdi

2.1.3 Textural and sensory properties of "***thabdi"***

The textural properties of *"thabdi"* are greatly influenced by its composition, type and the quality of the milk or khoa used for its preparation. The analysis of the textural profile of market samples of *"thabdi"* as reported by Komal (2010) revealed a large variation in the samples collected from different places. The hardness value of the sample varied from 6.013 to 220.771N. The variations in other properties have been reported as Stiffness: 1.27 to 310 N/mm, Adhesiveness: 3.269 to 60.616 N mm, Cohesiveness: -0.095 to 0.132, Springiness: 0.598 to 24.534 mm,

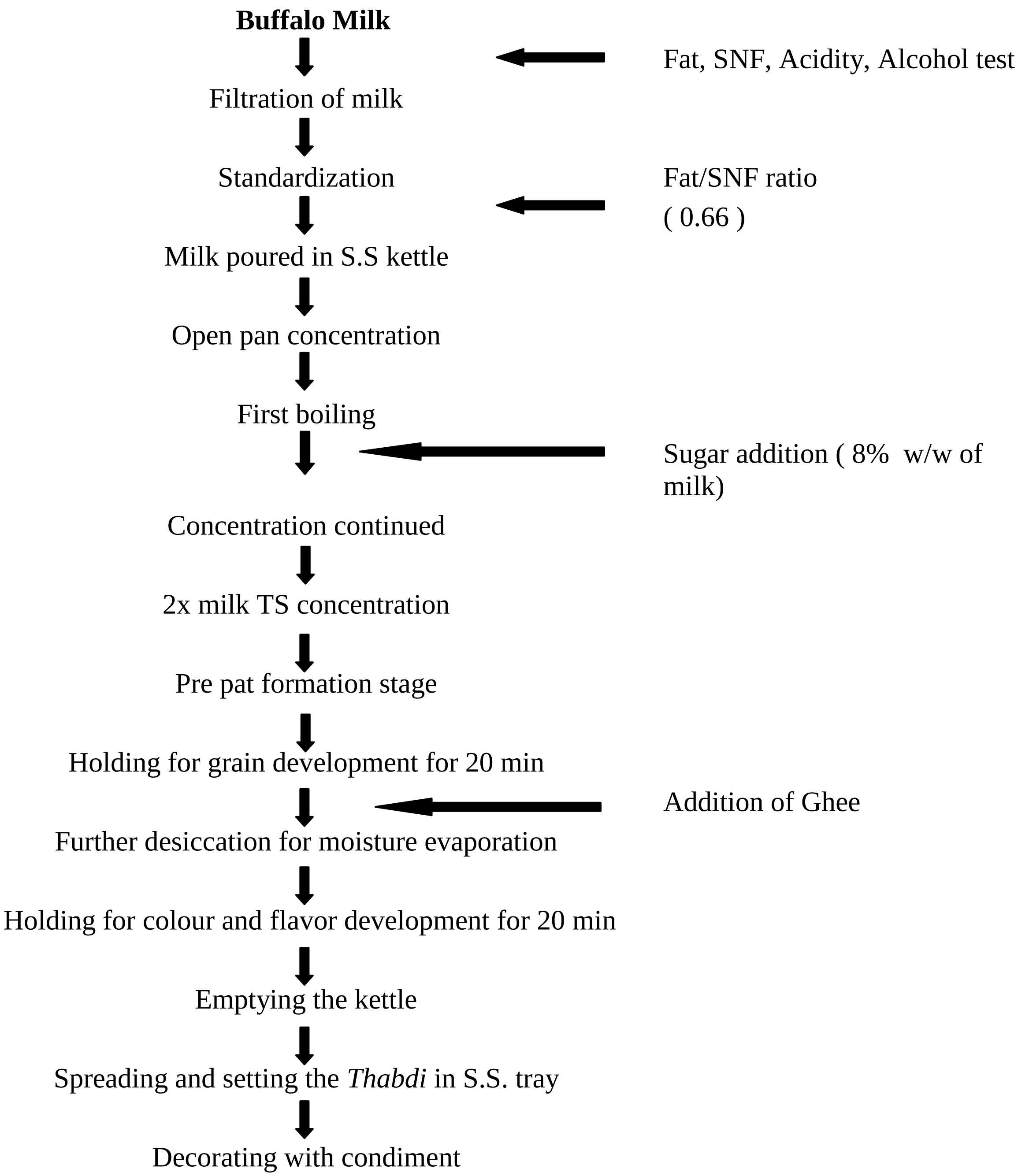

Fig. 2.1 Process flow diagram for *"thabdi"* manufacturing

Gumminess: -0.101 to 6.951 N, Chewiness: -5.63 to 60.2 Nmm and fracture force varied from: - 0.388 to 130.0 N.

The textural properties of *"thabdi"* prepared by the standardized process is reported to have Hardness 66.04 N, Cohesiveness 0.053, Springiness 3.23 mm, Chewiness 36.45 N-mm, Stiffness 22.74 N/mm, Adhesiveness 9.39 N-mm, Gumminess 4.76 and Fracture force 30.47 N respectively.

The sensory attributes most preferred in market *thabdi* are yellowish brown to dark brown colour, firm to slightly loose grainy texture having small pools of melted fat or a smear of solidified fat on the surface and cooked, rich nutty, ghee like flavor. It is available in the form of small rectangular shaped pieces or in a loose mass.

2.2 Concept of water activity

Water is the most abundant constituent found in the natural food. Since long time moisture content in food material is controlled by either eliminating water content or binding it so that food is stable to both microbiological and chemical deterioration. Simplest way of expressing such a status is water activity. Water activity and sorption behavior are two most powerful concepts available for understanding and controlling shelf life of foods (Labuza, 1968). Water activity is a physical measure of active water available in foods. For moisture sensitive dairy and food products, especially dehydrated products water is most important characteristics that affect the physical, chemical, microbial and sensory properties. It is a state of water rather than total water content, which is important as far as microbial proliferation is concerned. It has been reported that the state of water is related to vapour pressure of food. Greater the proportion of free water present greater is vapour pressure and vice versa. Increased bound water reduces vapour pressure (Scott, 1957).

Definition of water activity is based on the chemical potential of water within a food system, which at equilibrium must be same as the chemical potential of water in the surrounding of food. Hence water activity can be defined as the ratio of vapour pressure of water in food and vapour pressure of pure water at same temperature and pressure conditions (Labuza, 1968).

At equilibrium water activity is related to relative humidity of the surroundings atmosphere by the following equation

$$\mathbf{Aw} = \frac{\mathbf{P}}{\mathbf{P_o}} = \frac{\mathbf{ERH}}{\mathbf{100}} \qquad \ldots\ldots(2.1)$$

Where,

P = vapor pressure of water in food material at any given temperature
P_o = vapor pressure of pure water at that temperature

ERH= Equilibrium Relative Humidity

2.2.1 Moisture sorption isotherm

Sorption isotherms in food are of special interest in food preservation. When food is kept in different relative humidity, it adsorb or desorb moisture depending on its water activity (Kapsalis, 1987). When water activity is less than the surrounding humidity, product will absorb moisture and when reverse is the case it will desorb moisture. Product when equilibrated with different relative humidity, the water content in product on solid basis plotted on ordinate against the value of humidity on abscissa gives sorption isotherm of product. When fresh product with high water activity is kept at different humidity it desorbs moisture and corresponding isotherm is called desorption isotherm. But when the same product is first freeze dried and equilibrated at different humidity it adsorbs moisture. The corresponding isotherm is known as adsorption isotherm.

Brunauer *et al.* (1938) described five types of isotherms. Type-I is the well known Langmuir isotherm, obtained assuming monomolecular adsorption of gas by the porous solids in a finite volume of voids. Type-II is the sigmoid isotherm obtained for soluble products, which exhibits asymptotic trend as water activity approaches to one. Type-III known as Flory-Higgins isotherm, accounts for a solvent or plasticizer such as glycerol above the glass transition temperature. Type- IV isotherm describes adsorption by a swell-able hydrophilic solids until a maximum of hydration sites are reached. Type-V is a BET multilayer adsorption isotherm, observed for adsorption of water vapour on charcoal. Most of the food products generally show type-II isotherm having sigmoid shape (Iglesias and Chirife, 1976).

The characteristics of the moisture sorption isotherm could be explained by dividing it into three zones as shown in Fig. 2.2

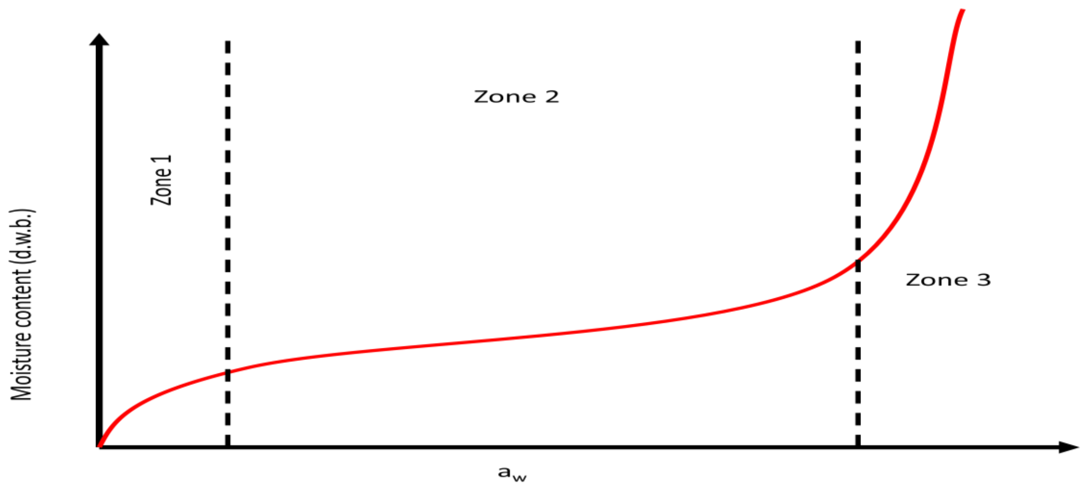

Fig. 2.2 Moisture sorption isotherm

Zone I describes the strongly bound water with an enthalpy of vaporization higher than that of pure water. In many aspects it behaves essentially as a part of solids. Moisture content in this region is unavailable for deterioration. This region is also termed as monolayer moisture region. It ranges up to 5-10% of moisture content on dry matter basis. Zone II represents water fraction less firmly bound than the first. It represents multilayer adsorption region and it extends up to a point where isotherm shows a rapid increase in the moisture content. Zone III water is more or less free water mechanically entrapped in the void spaces of the systems, having nearly all properties similar to those of bulk water. This region represents capillary condensation region where water condenses in porous structure of foods. This water acts as solvent for various solutes.

Moisture sorption isotherm illustrates steady-state amount of water held by the food solids as a function of a_w at constant temperature (Labuza, 1968). Moisture sorption isotherm is an extremely valuable tool for food scientists since it can be used to predict which reactions will decrease stability at a given moisture; it allows for ingredient selection to change the a_w to increase stability and can be used to predict moisture gain or loss in a package with known moisture permeability (Bell and Labuza, 2000).

Advantages of establishing moisture sorption of product are:

a) Water activity of product can be calculated at any moisture content and temperature

b) Bound water, capillary water and multilayer water can be estimated

c) Thermodynamic properties of product such as enthalpy, Gibbs free energy and heat of sorption can be computed.

2.2.2 Moisture sorption isotherm of milk products

Heldman *et al.* (1965) measured adsorption and desorption isotherms for skim milk powder in the temperature range between 2^0C and 38^0C with the relative humidity ranging from 20% to 90%. They obtained typical sigmoid curve with a hysteresis effect between the adsorption and desorption, which was most pronounced at relative humidity's bellow 45%.

Berlin *et al.* (1968) determined sorption isotherm data for milk powder components. The isotherm obtained for lactose free skim milk powder was smooth, sigmoid type II isotherm according to BET classification. The curve of lyophilized milk showed a break at water activity 0.5.

Sawhney *et al.* (1989) studied the water activity modification in heat concentrated whole milk product khoa using propylene glycol. The water activity at 0, 2, 4, 6 and 8% concentration were found to be 0.96, 0.948, 0.931, 0.904 and 0.901 respectively. GAB equation gave the best fit for it.

Kumar and Venugopal (1991) obtained the sorption curve for spray dried infant food found to be sigmoid in shape or type II according to the BET classification. The moisture sorption curve of roller dried infant milk food was similar to to spray dried product but in general it was observed that roller dried milk food had lower equilibrium moisture content at all relative humidities.

Sawhney *et al.* (2000) determined the adsorption and desorption isotherm of khoa at 25 and 45^{0}C. No discontinuities were observed and data showed a sigmoid shape of type II isotherm according to B.E.T classification. The equilibrium moisture content rose gradually at lower water activity (0.15-0.45 for adsorption and 0.15-0.75 for desorption) and a steep rise occurred above 85% relative humidity during adsorption as well as desorption.

Rao and Dhas *et all* (2004), reported the equilibrium moisture contents (EMC) of chhana podo using the static gravimetric method, at 5ºC and 35 ºC, over a range of water activity from 0.23 to 0.98. The isotherms obtained were of sigmoid shape, and of BET type II classification. The EMC at a given water activity was found to decrease as the temperature increased from 5ºC to 35ºC. Amongst the 12 sorption models tested, the Cauries model best described the EMC/water activity relationship of chhana podo by giving a closest fit to the experimental sorption data.

Ramkrishna *et al., (*2004) determined the sorption isotherm of milk burfi, one of the important Indian traditional milk based sweet, using sugar and sugar substitutes. The isotherm followed typical sigmoid shape.

Sahu (2005) studied the sorption isotherm of skim milk powder at 15^{0}C, 25^{0}C and 35^{0}C. The sorption data was subjected to seven different isotherm models and GAB model was found to be the best fitted equation. Monolayer moisture content of skim milk powder was 5.19g / 100g of solids at 15^{0}C, which decreased to 4.52g / 100g of solids at 35^{0}C.

Govardhan (2006) studied the sorption isotherm of gulabjamun mix powder (GMP) at 15, 25, 35 and 45^{0}C using a gravimetric-static method. Monolayer moisture content of GMP decreased from 0.1002g water/ g of solids at 15^{0}C to

0.0772g water /g of solids at 45^{0}C. The heat of sorption was found to increase initially with moisture content and attain a peak value of 8213KJ/Kg at around 9% moisture level and then decrease.

Das and Sahu (2009) studied the Moisture sorption isotherm of sandesh, one of the most popular milk products in India. The isotherms obtained were of sigmoid shape and of the Brunauer–Emmett–Teller type. Out of three sorption models fitted to the experimental data, Caurie's model was found superior in interpreting the moisture adsorption characteristics of sandesh.

Sawhney *et al.,*(2010) studied the moisture sorption characteristics of dried acid casein from buffalo skim milk at 25, 35 and 45ºC using a gravimetric-static method. Both the adsorption and desorption isotherms exhibited sigmoid shape corresponding to type II, typical to many foods. There was generally a negative temperature effect on equilibrium moisture content. The effect of temperature was, however, statistically not significant over the temperature range of 25 to 45ºC. Of the seven sorption models tested for fitting the sorption data, the GAB model gave the best fit at all the three temperatures.

Pagire. (2011) studied the effect of moisture sorption isotherm on khoa/ peda at 15, 25 and 35^{0}C. There was increase in the equilibrium moisture content with the increase in water activity. It showed sigmoid in shape type II isotherm, and the GAB model gave the best fit at all the three temperature effects.

2.2.3 Isotherm models

The relation between moisture content and a_w is not linear, but sigmoid which makes the prediction of a_w from moisture content difficult. Various mathematical models have been proposed in literature to describe sorption isotherms. Some were developed with a theoretical basis to describe adsorption mechanism e.g. BET and GAB (Brunauer *et al.*, 1940; Van den Berg and Bruin, 1981) whereas others are just empirical or a simplification of more elaborate models. In some ranges of water activity, sorption isotherm can be approximated to linear equations.

Chirife and Iglesias (1978) reported that models proposed by Halsey (1948) and Oswin (1946) are the most versatile two-parameter equations for describing the sorption isotherms. Caurie (1981) developed a model which could help in evaluating properties of sorbed water. Mizrahi and Karel (1977) proposed a three parameter model that yielded a good fit for moisture sorption isotherms of several foods. In the COST 90 project on water activity, Bizot (1983) demonstrated that the 'Guggenheim-Anderson-de Boer' (GAB) equation was the three parameter theoretical model giving best fit for most food isotherms over a wide water activity range and also provides a better evaluation of the amount of water tightly bound by primary adsorption sites. Singh and Singh (1996) discussed the application of GAB model for water sorption isotherms of food products.

Water sorption isotherm at 30ºC of pre cooked beef previously dried at three different temperatures was determined by Iglesias and Chirife in 1976. It was found that Halsey equation represents adequately the sorption behavior obtained in the water activity range of 0.10 – 0.80 by Iglesias and Chirife in 1976.

Modified Henderson and Chung-Pfost equations were good for fibrous and starchy materials while the modified Halsey fitted well for high oil and protein materials. A study by Mazza and Jayas (1991) revealed that Guggenheim-Andersons-De Boer (GAB) model was superior to three other models (Chung-Pfost, Halsey and Henderson) in characterizing the sorption behavior of sunflower seed, hulls and kernels. In case of fruits, Iglesias and Chirife (1976) equation was found best fitted. The Halsey equation gives the best fit for meat followed by Oswin equation (1946). For milk product Halsey equation gives the best description of the experimental data followed by Kuhn equation. Mizrahi equation gives a fair description of this group of foods. Oswin, Kuhn, Iglesias and Chirife equations show reasonably good fit to the experimental data (Boquet *et al.* 1978).

Sawhney *et al.* (1991) determined moisture desorption isotherm of khoa at 25, 35 and 45ºC. It was found that GAB equation has better fit compared to other models.

Prateek (2003) studied the desorption isotherm of ready to use Basundi mix in the temperature range of 5-45ºC exhibited the sigmoid shape corresponding to type II. Modified Mizrahi followed by GAB were found to be best fitted at all temperatures.

Sawhney *et al.,* (2010) studied the moisture sorption characteristics of buffalo skim milk powder at 25, 35 and 45ºC over a water activity range of 0.11 to 0.97. Adsorption isotherm exhibited sigmoid shape corresponding to type II. GAB model gives the best fit for the sorption data of buffalo skim milk powder at all the three temperatures. Temperature dependence of GAB parameters has been determined in the form of Clausius-Clapeyron equation. The monolayer moisture content decreases with increase in temperature.

2.3 Temperature dependence of moisture sorption isotherm

The knowledge of temperature dependence of sorption phenomenon provides useful information on the energetics of water sorption process in foods (Rizvi, 1995). The net isosteric heat is useful in estimating the state of adsorbed water by solid particles, which is a measure of the physical, chemical and microbial stability of food in storage (Labuza, 1968). The monolayer moisture content depends on the temperature at which the isotherm was established. In general, monolayer values decrease with increasing temperature of equilibration.

Shift in water activity by temperature at constant moisture content is due to change in water binding (increased mobility of water), dissociation of water or increase in solubility of solute in water (Labuza *et al.,* 1985). Because of the nature of water binding, at constant water activity most food holds less water at higher temperature.

Moisture content at equilibrium usually decreases with increase in temperature. For constant moisture contents, the amount of bound water is also more easily desorbed with increase in temperatures, wherein mobility of the water molecules as well as dynamic equilibrium between vapor and adsorbed phase are affected.

Effect of temperature on increasing the water activity at constant moisture content is greatest at lower to intermediate water activities. In some cases, such as sugar rich products like fruits, there is an inversion effect. This is because of the increased solubility of sugar. The solubilization reduces the mobility of water. The cross over point depends on the sugar content, higher the sugar content lower the inversion point. This point varies from a_w 0.55 to 0.75.

Labuza (1984) showed that the effect of temperature on Aw is negligible in high moisture foods, but in intermediate and low moisture foods, a 10ºC change in temperature can result in small percentage change in water activity.

Isotherms for whey protein isolates (WPI), high miceller protein and milk protein concentrate powders have been reported by Foster *et al.,* in 2005. The isotherm data for WPI powder measured at 4, 20, 37 and 50ºC did not show any temperature dependence in the isotherms up to a water activity of about 0.6. it also showed the effect of temperature was greatest when compared at 50ºC.

Prateek (2003) studied the effect of temperature on desorption isotherms of ready to use *Basundi* in the temperature range of 5-45ºC. The isotherm showed inversion at higher temperatures and adsorbed proportionately more moisture towards the later parts of curve particularly above 0.70 Aw. Monolayer moisture contents of Basundi mix formulation were in the range of 2.11 to 3.58 g/100g solids.

2.4 Isosteric heat of sorption

Differential enthalpy of food relates to concentration of water in food to its partial pressure, which is crucial in analysis of heat and mass transport phenomena during dehydration. They determine the end point to which a food must be dehydrated to achieve a stable product with optimal moisture content, and minimal amount of energy required to remove a given amount of water from the food (Aviara and Ajibola, 2002)

The net isosteric heat of sorption is defined as the amount of energy by which the heat of vapourization of moisture in a product exceeds the latent heat of pure water (Labuza, 1968). It gives a measure of the water-solid binding strength. The isosteric heat is strongly dependent on moisture content. Isosteric heat of sorption provides information of the state of sorbed water and thus a measure of physical, chemical and microbiological stability of food material under a given storage condition can be know.

Isosteric heat of sorption or the differential entalphy can be determined by Clausis-Clapeyron equation:

$$ln\frac{A_{wT_1}}{A_{wT_2}} = \frac{Q_s}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

………..(2.2)

Where, A_w = water activity at respective temperature

Qs = Isosteric heat of sorption (Kcal/mol of water)

R = Gas constant (8.314 J/˚C. mole)

Knowledge of isosteric heat of sorption is of a great importance when designing equipment for dehydration process. This is due to the fact that the heat of vaporization of sorbed water may increase to values above the heat of vaporization of pure water as food dehydrated to low moisture levels (King, 1968).

Thermodynamic calculations based on the Clausis-Clapeyron equation have been used to estimate the enthalpies of sorption and desorption. In general, enthalpy decreases as water activity increases. For example in ovalbumin the enthalpy decreased rapidly from -600 to approximately -100 Kcal/mol water as moisture content increased from 0.05-0.39 g water/100g proteins (Kuntz and Kauzman, 1974).

The effect of temperature on increasing the water activity at constant moisture content is greatest at lower to intermediate water activities. In some cases, such as sugar rich products like fruits, there is an inversion effect. This is because of the increased solubility of sugar. The solubilization reduces the mobility of water. The cross over point depends on the sugar content, higher the sugar content lower the inversion point. This point varies from a_w 0.55 to 0.75.

Iglesias and Chirife (1976) studied the adsorption isotherm of pre cooked dried beef at 30ºC and 50ºC. It was found that the quantity of sorbed water at a given relative humidity increased as the temperature was increased. The net isosteric heat was calculated using the Clausis-Clapyeron equation. The decrease in net isosteric heat with the amount of water sorbed was observed.

Labuza (1984) showed that the effect of temperature on Aw is negligible in high moisture foods, but in intermediate and low moisture foods, a 10ºC change in temperature can result in small percentage change in water activity.

Sawhney *et al.* (1991) studied the moisture sorption of *khoa* at three different temperatures over a water activity range of 0.11-0.97. The water activity of khoa increased with increasing temperature up to 0.90. Above this, effect of temperature on water activity diminished. The monolayer moisture content of khoa decreased with increasing temperature. The net isosteric heat of khoa decreased rapidly until a moisture level of 0.1g/g solids and approached a constant value of 0.43KJ/mole above a moisture level of 0.25g/g solids.

2.5 Moisture sorption hysteresis

Adsorption isotherm is obtained by placing a completely dry material in the various atmospheres of increasing relative humidity and measuring the weight gain due to moisture. Similarly, desorption isotherm is obtained wet sample under same relative humidity and measuring the loss in weight due to water. The difference between desorption and adsorption isotherm is known as moisture sorption hysteresis. Moisture sorption hysteresis is the phenomenon according to which two different paths exist between adsorption and desorption isotherm. If one plots the amount of water per unit mass of solids in the ordinate and the corresponding relative humidity on the abscissa. The desorption isotherm usually lies above the adsorption isotherm and a closed hysteresis loop is formed (Kapasalis, 1981).

Generally type C hysteresis is found in food where loop extends over the entire water activity range. Hysteresis in food varies depending upon the type of food product and temperature. At higher temperature hysteresis loop decreases ie. span limits and so the amplitude of loop decreases. Hysteresis can change due to several factors like temperature, denaturation of protein at higher temperature, changes in crystalline structure of sugar, rupturing of hydrogen bonds providing more number of sorption sites and compression or cavitation in foods.

Moisture sorption hysteresis is a phenomenon according where two different paths exist between adsorption and desorption isotherm. If one plots the amount of water per unit mass of solids in the ordinate and the corresponding relative humidity on the abscissa. The desorption isotherm usually lies above the adsorption isotherm and a closed hysteresis loop is formed (Kapasalis, 1981).

Moisture sorption hysteresis has important theoretical and practical implications in foods. The practical implication deals with the effect of hysteresis in chemical and microbiological deteriorations. Due to hysteresis a much lower vapour pressure is required to reach a certain amount of water by desorption than adsorption (Kapsalis, 1987). Interestingly, Acott and Labuza in 1975 had shown that a few fungi and bacteria grew rapidly in the system prepared by desorption process than by adsorption at same water activity.

Depending on the type of food and temperature, variety of hysteresis loop shapes can be observed. In high sugar or high pectin foods, hysteresis mainly occurs at below the monolayer region (Okos *et al.,* 1992). In high protein foods, the phenomenon is extended through an Aw of about 0.85 (Kapsalis, 1981). Overall, total hysteresis decreases as sorption temperature increases (Wolf *et al.,* 1972).

Iglesias and Chirife (1976) stated that for some foods like rice, chicken, tapioca etc. increasing temperature decreases hysteresis while for some foods like ginger and nutmeg, the total hysteresis remained constant or even increased in spices like cinnamon, anise, coriander etc, the magnitude of the hysteresis loop is reported to be affected by composition and structure and hydration or dehydration history (Berlin, 1981).

Hysteresis in food is mainly due to the porous nature of food. Four theories have been put forward in order to explain hysteresis phenomenon based on porous nature of foods, namely incomplete wetting theory, ink bottleneck theory, open pore theory, and Domain theory. Hysteresis in biopolymer is generally attributed to a deformation of the polypeptide chain with in the protein molecule as the polar absorbents occupy suitable position for hydration binding or dipole interaction (Kapsalis, 1987).

Sawhney *et al.* (2000) studied the hysteresis effect of *khoa* at temperatures 25 and 45ºC. It was moderate for water activity less than 0.1. It increased at high water activities and occurred primarily in the water activity range of 0.35 to 0.65 at both 25 and 45ºC. The hysteresis effect diminished beyond 0.8 water activity and the adsorption and desorption isotherm of khoa coincided with each other at water activity above 0.96 at 25ºC and above 0.90 at 45ºC. The hysteresis effect was moderate in monolayer moisture content region of khoa.

CHAPTER – 3

Materials and Method

3.0 MATERIALS AND METHOD

The methods followed and the materials used in carrying out the proposed dissertation work on establishing the moisture sorption characteristics of “thabdi” has been explained under the following headings:

3.1 Preparation of test sample of *thabdi*

3.2 Determination of chemical composition of *“thabdi”*

- 3.2.1 Determination of moisture
- 3.2.2 Determination of fat
- 3.2.3 Determination of protein
- 3.2.4 Determination of sugar (reducing and non reducing)
- 3.2.5 Determination of titrable acidity
- 3.2.6 Determination of total ash

3.3 Establishing moisture sorption isotherm

- 3.3.1 Sorption apparatus
- 3.3.2 Selection of salts for maintaining different humidity
- 3.3.3 Maintenance of temperature
- 3.3.4 Sorption procedure

3.4 Fitting of isotherm equation

- 3.4.1 Accuracy of fit
- 3.4.2 Calculation of net isosteric heat
- 3.4.3 Temperature dependence of isotherm parameters

3.5 Evaluation of moisture sorption hysteresis

- 3.5.1 Hysteresis amplitude
- 3.5.2 Hysteresis unit
- 3.5.3 Total hysteresis energy

3.6 Statistical analysis

- 3.6.1 Two way ANOVA
- 3.6.2 Paired t-test

3.1 Preparation of test sample of *thabdi*

"Thabdi" prepared from buffalo milk was chosen as test sample for present study. Test sample of "thabdi" was prepared in jacketed steam kettle by using the standardized method given by Krupa *et al*., 2011 (Fig. 3.1)

Fresh Buffalo milk was obtained from Experimental Dairy Plant of National Dairy Research Institute, Karnal for the preparation of thabdi. Fat, SNF, Acidity and Alcohol test are carried out. Milk was then filtered and taken in SS Kettle. Milk was standardized to Fat:SNF ratio of 0.66. Open pan concentration was carried out, sugar is added @8% by weight of milk at the first boiling stage and the concentration was continued till pre-pat formation stage. After 20 minutes holding, ghee was added @1.2% to it and further desiccation is carried out for moisture evaporation. Again it is held for 20 minutes for colour and flavor development. Fig. 3.1 shows the different intermediate stages of thabdi preparation. The thabdi test samples are shown in fig. 3.2.

3.2 Determination of chemical composition of "thabdi"

3.2.1 Determination of moisture content

The moisture content (%w.b.) of the *Thabdi* samples was determined by standard procedure using Mojonnier Milk Tester Model-D **(Laboratory Manual, 1959).**

Approximately 3.0 gm of *Thabdi* sample was weighed in a clean and dried moisture dish. 2-3 ml of hot distilled water was added to the sample to make a paste, which was spreaded over the entire bottom of the dish. The dish was then placed on a hot plate at 180^0C and heated till colour of residue become light brown. The dish was then transferred to the total solids vacuum oven at 100^0C, where it was heated for 20 minutes under not less than 50 cm of vacuum. Finally the dish was transferred to desiccator (containing calcium chloride) for cooling, followed by subsequent weighing.

Initiation of grain formation after addition of sugar.

Holding for 20 minutes in S.S. Kettle for grain development

Again holding for 20 minutes for further moisture removal after addition of ghee.

Setting thabdi in tray to allow it to cool

Fig. 3.1 Intermediate stages of thabdi processing

Fig. 3.2 "Thabdi" prepared from buffalo milk

The percent moisture in *Thabdi* sample was calculated by using the following equation:

$$\text{Moisture (\% w.b.)} = \frac{\text{Loss in weight of sample}}{\text{Weight of sample taken}} \times 100 \qquad \textbf{(3.1)}$$

3.2.2 Determination of fat

Fat extraction of *Thabdi* was determined as per the procedure described in **IS: 2311-1963**.

One gram of sample was weighed in a Mojonnier fat extraction tube. 1 ml of Concentrated Ammonia was added to it and mixed in lower bulb of the fat extraction tube, followed by addition of 10 ml ethyl alcohol and 25 ml diethyl ether. The tube was closed tightly and the contents were vigorously shaked. The tube was then opened and 25 ml of light petroleum ether was added followed by shaking for 1 min, and then centrifuging for 5 min. The supernatant was decanted into previously dried, cooled and weighed dish. The extraction and decantation operation was repeated twice by using 15 ml diethyl ether and 15 ml petroleum ether. The solvent was dried on hot plate and after complete dehydration; dish was placed in an oven at 100^{0}C for 1 hr. The dish was cooled and then weighed and the per cent fat was calculated using following equation:

$$\text{Fat (\% by weight)} = \frac{\text{Weight of residue}}{\text{Weight of sample}} \times 100 \qquad \textbf{(3.2)}$$

3.2.3 Determination of protein

Total nitrogen/protein of *Thabdi* was determined by semi-microkjeldahl method **(IS: 1479-Part-II, 1961)**, using Kjel-plus digestion system (Model-KPS 006L, M/s.Pelican Instruments, Chennai) and Kjel-plus semi-automatic distillation system (Model-Distil M, M/s.Pelican Instruments, Chennai) as follows:

In a digestion tube 0.5 – 1.0 g of the sample was accurately weighed and then 2.4 g of digestion mixture (potassium sulphate: copper sulphate: selenium dioxide; 1:0.1:0.1) was added. To the tube contents, 10 ml of nitrogen-free concentrated sulphuric acid was added. The tubes were then transferred to the digestion block, where the contents were digested for about 30 min at a final temperature of 350^{0}C.

The cooled, digested contents were loaded in the Kjel-plus distillation unit and after the unit was ‘ready’, a fixed volume of alkali (20 ml of 40 per cent sodium hydroxide) was added automatically to the sample. The distillation time was fixed at 3 min. The liberated ammonia was condensed and collected in 25 ml of saturated boric acid solution containing three drops of mixed indicator [equal volume of saturated solution of methyl red and 0.1 per cent methylene blue solution, both made in 95 per cent (v/v) ethanol]. The distillate in boric acid was titrated against 0.05 N sulphuric acid. A reagent blank was simultaneously run using all the above chemicals except the sample and its reading was subtracted from the experimental reading. The per cent total nitrogen was calculated using the equation:

$$\% \text{ total nitrogen} = \frac{0.07 \times (\text{Burette reading} - \text{Blank reading})}{W} \quad \ldots\ldots \textbf{(3.3)}$$

Where, W=Weight of sample

For converting the values of total nitrogen into per cent total protein, the values were multiplied by a factor of 6.38.

3.2.4 Determination of sugar (reducing and non-reducing)

Reducing (lactose) and non-reducing (sucrose) were determined by the volumetric method specified for ice-cream in **BIS (IS 2802, 1964)**.

In a 250 ml conical flask, 25 g *Thabdi* sample was transferred and diluted with 150 ml lukewarm water. The contents were mixed and precipitated with neutral lead acetate solution and one drop of alumina cream. After 15 minutes, the excess lead acetate solution was precipitated with sufficient saturated sodium oxalate solution and the contents were filtered through Whatman No.1 filter paper in 250 ml volumetric flask. The precipitates on the filter paper were washed with hot water and the washings were collected in the volumetric flask. After cooling the flask, the volume was made up to 250 ml with distilled water.

i) Lactose (Reducing Sugar)

The filtrate, which comprised of the sugar solution, was filled in the burette and titrated against a mixture of 5 ml each of Fehling's A and Fehling's B solutions using methylene blue as an indicator. The titration was carried out in boiling condition over a flame and end point was observed as clear brick red precipitates. The readings were then used to compute lactose content of the product as follows:

$$\text{Reducing sugar (Lactose) (\%)} = \frac{67.8}{X} \quad \ldots\ldots\ldots \textbf{(3.4)}$$

Where, X = ml of filtrate required to titrate Fehling's A+B solution

ii) Sucrose (Non-Reducing Sugar)

Ten ml of filtered solution (prepared as described in 3.2.3) was hydrolyzed using 1 ml of concentrated hydrochloric acid in boiling water bath for 5 minutes. It was cooled immediately and contents were neutralized with 1 N sodium hydroxide solution. This content was quantitatively transferred to 250 ml volumetric flask and the volume was made up to mark. Then this solution was used for titration against boiling 5 ml each of Fehling's A and B solution as usual and from the average titration values, the percentage sucrose was determined as under:

$$\text{Non-Reducing sugar (\%)} = \left(\frac{6500}{Y} - \frac{2500}{X}\right) \times 0.4 \times \text{Factor} \qquad \textbf{…………(3.5)}$$

Where,

X = burette reading (ml) of reducing sugar as in 3.2.3.1

Y = burette reading (ml) of filtrate titrated with Fehling's A+B solution

Factor = Standard sugar solution titrated with Fehling's A+B solution. The values ranged between 52.2 and 52.35 ml.

- Standard sugar solution was prepared as given in BIS Handbook (BIS: Part XI, 1981).

3.2.5 Determination of titrable acidity

A.O.A.C (1975) method for cheese was adopted for *thabdi* for determining acidity in terms of percent lactic acid. Two gm of *thabdi* sample was weighed into a porcelain dish. The product was rendered into a fine paste using 3 ml of hot distilled water (65ºC). The contents were again diluted by another 17 ml of hot distilled water washing off the adherents from the pestle. Ten ml of 0.1 N NaOH was added and the content was mixed thoroughly. Titration was done against 0.1N HCl acid with continuous stirring after adding 1 ml of 0.5% phenolphthalein indicator till the pink color disappeared completely. Acidity was expressed as lactic acid per 100 gm of *thabdi*.

$$\text{Lactic Acidity } (\%) = \frac{10-V}{W} \times 0.9$$

……. **(3.6)**

Where,

V = Volume of 0.1 N HCl required for titration

W = Weight of *Thabdi* sample

3.2.6 Determination of total ash

Ash content of all the samples was determined by procedure described in **BIS (IS: 1547-1985)**. Two to three grams of homogenous sample was weighed in a silica crucible. The sample in crucible was heated on naked-flame till it was completely reduced to ash. The sample was then transferred to muffle furnace and held for 3.5 hrs at 550±2^{0}C. After cooling in the desiccators, the crucible was weighed. The process was repeated till constant weight. The total ash content in per cent was calculated as follows:

$$\text{Total ash (\% by weight)} = \frac{100\,(W_2 - W)}{(W_1 - W)}$$

…(3.7)

Where,

W = Weight in g of the empty crucible

W_1 = Weight in g of the crucible with sample

W_2 = Weight in g of the crucible with ash

3.3 Establishing moisture sorption isotherm

3.3.1 Sorption apparatus

The standard sorption apparatus recommended by COST 90 project **(Wolf *et al., 1985*)** was used in equilibration study. The sorption apparatus (shown in fig. 3.3 and 3.4) consisted of a wide mouth glass bottle (200 ml) with vapor tight lid used as sorbostat. Inside each sorbostat there was a support for weighing beaker (25 ml) and the weighing beaker (10 ml) in which the sample material was exposed to the humid atmosphere in the container maintained by the saturated salt slurries.

Fig. 3.3 Sorption Apparatus

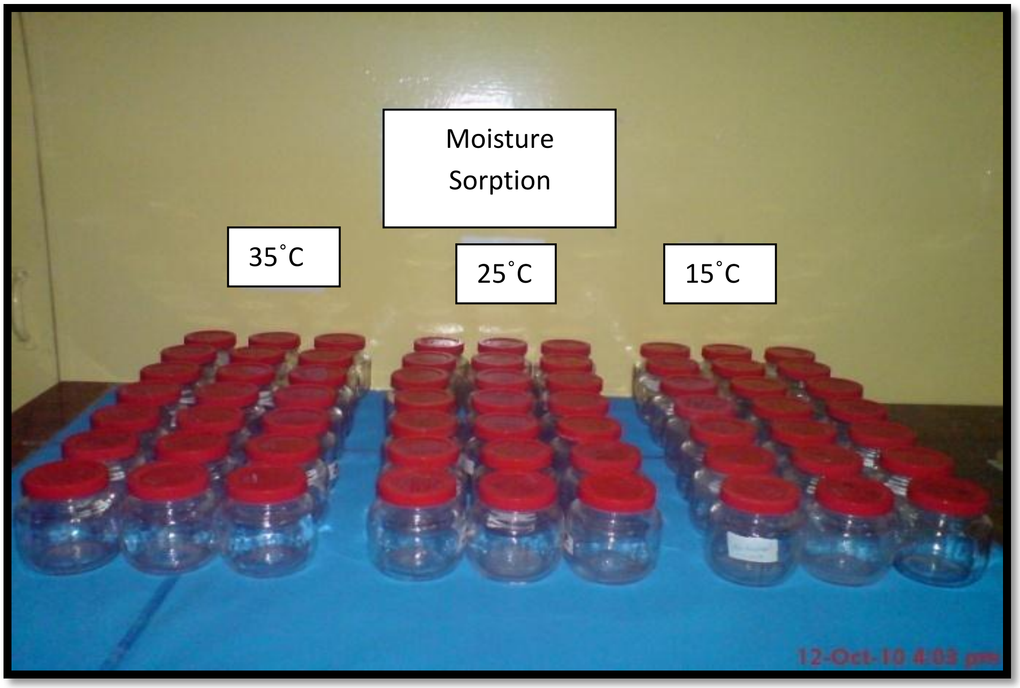

Fig. 3.4 Sorption apparatus arranged at different temperatures

Fig. 3.5 Constant temperature oven

3.3.2 Selection of salts for maintaining different humidity

Eight reagent grade salt slurries namely, lithium chloride, magnesium chloride, potassium chromate, magnesium nitrate, sodium chloride, potassium chloride, potassium nitrate and potassium sulphate were chosen (Greenspan, 1977). The salts were dissolved in distilled water at 60ºC and then cooled to the test temperatures (15, 25 and 35ºC) for crystallization to form saturated slurries. Water activities of these salts ranges from 0.11 to 0.97 at different temperature are given in table 3.1.

Table 3.1 Water Activity of Salts at Different Temperature

Salts	Water Activity		
	15ºC	25ºC	35ºC
$LiCl.H_2O$	0.113	0.113	0.1125
$MgCl_2.6H_2O$	0.333	0.328	0.320
K_2CO_3	0.431	0.432	0.432
$Mg(NO_3)_2.6H_2O$	0.559	0.529	0.499
NaCl	0.756	0.753	0.749
KCl	0.817	0.810	0.802
KNO_3	0.953	0.936	0.907
K_2SO_4	0.979	0.973	0.967

3.3.3 Maintenance of temperature

A set of three temperatures viz; 15, 25 and 35ºC were selected for the study. Constant temperature oven (Fig. 3.5) were used for maintaining these temperatures. Effect of temperature on water activity of *thabdi* was studied by comparing moisture gain or loss of sample inside the sorbostats at different water activity and at corresponding temperatures.

3.3.4 Sorption procedure

Gravimetric method recommended by COST-90 project was followed in the sorption procedure. The sorption apparatus were allowed to equilibrate at respective temperatures for four days before samples were placed into them. For adsorption isotherm, the samples were completely dehydrated by placing them over Phosphorous Pentoxide (P_2O_2) for 20 days. Weighed quantity of dried sample (Approx. 1gm) was taken into tared sample beakers, which was then transferred to the sorption apparatus, containing saturated salt slurries. Experiment was conducted in triplicates for best results. The sorption apparatus containing samples were kept at temperatures of 15, 25 and 35ºC.

Samples were hydrated in desiccators over distilled water at room temperature to approximately 40% (dry basis) moisture content to obtain desorption isotherm.

To prevent mold growth, about 0.1mg of potassium sorbate was added to each "*thabdi*" sample. The samples were weighed at intervals of 3 days and equilibrium was judged to have been attained when difference between three consecutive sample weighing was less than 0.001gm. The equilibrium period ranged from 12 to 14 days. During this period, the mold growth was observed for the sample at a_w of 0.97 and hence it was discarded. Equilibrium moisture content (EMC) in terms of gm of water/100gm of solids was obtained for each sample by using equation 3.5. The EMC were plotted against relative humidity to establish moisture sorption isotherm.

$$M = \frac{(\mathrm{W2} - \mathrm{W1}) + \mathrm{m}}{(\mathrm{W1} - \mathrm{m})} \times 100$$

…….. **(3.8)**

Where,

M = Equilibrium Moisture Content (g water/ 100 g of solids)

W_1 = Initial weight of sample (g)

W_2 = Final weight of sample (g)

m = Initial Moisture content of sample (g, d.b.)

3.4 Fitting of isotherm equation

The isotherm equations that were used to fit the data are presented below. The linearized forms of the two and three parameter models were used for evaluating the best fitted values of constants using a linear regression programme. The sorption data was analyzed according to the models and the corresponding constants were determined. The goodness of fit of each model was computed in terms of root mean square percent error (RMS %).

HASLEY

$$a_w = e^{\left[-a/W^b\right]} \quad \text{......} \quad (3.9)$$

OSWIN

$$W = a\left\{\frac{a_w}{1-a_w}\right\}^b \quad \text{......} \quad (3.10)$$

CAURIE

$$\ln\frac{1}{W} = \ln\frac{1}{CW_m} + \frac{2C}{W_m}\ln\frac{1-a_w}{a_w} \quad \text{.....} \quad (3.11)$$

MODIFIED MIZRAHI

$$W = \frac{a + a_W(ca_W + b)}{a_W - 1} \quad \text{.....} \quad (3.12)$$

GAB

$$W = W_m \frac{Cka_w}{(1-ka_w)[1-ka_w+Cka_w]} \quad \text{......} \quad (3.13)$$

Where,

W = Equilibrium moisture content (g/100g dry solids)

a_w = Water activity

a, b and c are constant

The GAB equation could be rearranged into second-degree polynomial equation

$$\frac{a_W}{W} = aa_w^2 + ba_w + c \qquad \text{...... (3.14)}$$

Where,

$$a = \frac{k}{W_m}\left[\frac{1}{C-1}\right] \qquad \text{..... (3.15)}$$

$$b = \frac{1}{W_m}\left[1 - \frac{2}{C}\right] \qquad \text{........... (3.16)}$$

$$c = \frac{1}{W_m Ck} \qquad \text{...... (3.17)}$$

The constants a, b and c significantly depends on the type of regression analysis and nonlinear least square procedure is considered the most reliable technique (Schar & Ruegg, 1985; Ramesh, 2003). Therefore nonlinear regression analysis of a_w/W vs a_w yields a polynomial equation of the second order. The coefficients a, b and c were thus obtained from this polynomial equation and then substituted one by one to obtain GAB constants W_m, C and K.

'W_m' is the moisture content corresponding to saturation of all primary adsorption sites by one water molecule (equivalent to monolayer in the BET theory), 'C' is the Guggenheim constant and 'k' is the factor correcting for properties of multilayer molecule with respect to the bulk liquid.

3.4.1 Accuracy of fit

The accuracy of fit was evaluated by calculating the root mean square percent error (RMS %).

$$RMS\% = \sqrt{\frac{1}{n}\left[\sum_{1}^{n}\left(\frac{w_{EXP} - w_{CAL}}{w_{EXP}}\right)^{2}\right]} \times 100 \quad \text{……. (3.18)}$$

Where,

W_{exp} = Experimental moisture content

W_{cal} = Calculated moisture content

n = Number of observations

3.4.2 Calculation of Net Isosteric Heat of Sorption

The net isosteric heat of sorption was evaluated from following generalized equation of Clausius - Clapeyron.

$$\ln\left(\frac{a_{wT1}}{a_{wT2}}\right)_{w} = \frac{\Delta Hw}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{……… (3.19)}$$

Where,

ΔH_w = Net isosteric heat of sorption

R = Gas constant (8.314 J/deg. mol)

The isosteric heat of sorption was calculated from above equation by plotting log (a_w) vs. 1/T and determining slope of curve which is equal to $-\Delta H/2.303R$. The slope of each line was found out by linear regression and net isosteric heat of sorption was calculated.

3.4.3 Temperature Dependence of Isotherm Parameters

Temperature dependence of sorption phenomenon provides the valuable information about the changes related to the energetic of the system. The constants in moisture sorption isotherm equations which represent either temperature or a function of temperature are used to calculate the temperature dependence of water activity.

Weisser (1985) proposed using the exponential relationship between GAB parameters (Wm, C, and k) and temperature to extend the GAB model to incorporate the temperature effect. The temperature dependence of isotherm parameters were thus determined by correlating the GAB (T) constants with temperature by using the following form of Arrhenius-type of equations:

$$W_m(T) = W'_m \, .e^{\Delta H'/RT} \qquad \dots (3.20)$$

$$G(T) = G' \, .e^{(H1-Hm)/RT} \qquad \dots (3.21)$$

$$K(T) = K' \, . \, e^{(HL-Hm)/RT} \qquad \dots (3.22)$$

Where,

H_1 = Total heat of sorption of the first layer on primary sites

H_m = Total heat of sorption of multilayer

H_L = Heat of condensation of pure water vapour

$\Delta H'$ = Partial molar enthalpy of sorption

W'_m, C' and K' are constants

The above equations together with GAB equation were used to calculate the equilibrium water content W(T) of *Thabdi* at known water activity and temperature by means of GAB(T) constants.

3.5 Evaluation of moisture sorption hysteresis

3.5.1 Hysteresis amplitude

The hysteresis amplitude for given water activity was characterized by relative water content difference between desorption and adsorption in the following form

$$A = (D-A) / D \qquad \text{.....(3.23)}$$

3.5.2 Hysteresis units

Adsorption values of moisture content was subtracted from desorption values at regular water activity interval of 0.1.

Resulting difference was plotted against water activity and graphical integration of area under the curve gave the hysteresis unit.

3.5.3 Hysteresis energy / Heat of sorption

The total hysteresis energy was determined from the generalized equation of following form described by Johnston and Duckworth (1985):

$$\Delta G = RT \int_{O}^{U} ln\, pdw \qquad \text{...........} \qquad (3.24)$$

Where,

ΔG = Free energy change per sorption cycle (KJ/mol)

p = Ratio of adsorption to desorption vapour pressure of sorbed water

U = Upper closure point of hysteresis loop

O = Lower closure point of hysteresis loop

W = Water content

A plot of RT.ln(p) against W gave a curve, the area under which represents the total hysteresis energy.

3.6 Statistical analysis

3.6.1 Two way ANOVA

Two way analysis of variance (ANOVA) was carried out using MS.Excel to check that whether there is any significant difference on equilibrium moisture content because of water activity and temperature at 5% level of significance.

3.6.2 Paired t-test

Paired t-test was carried out using MS.Excel for moisture sorption hysteresis to check whether there is any significant difference between the desorption and adsorption in the loop formed at 5% level of significance.

CHAPTER – 4

Results and Discussion

Present study was executed to find the moisture sorption characteristics of a traditional Indian dairy product "thabdi". Initially the compositional analysis is carried out of the product. Then the effect of moisture sorption isotherm on thabdi, its temperature dependence and differential enthalpy are discussed.

The results of the dissertation work carried out and its discussion are represented in the following sub-headings:

4.1 Compositional analysis of "thabdi"

4.2 Moisture sorption isotherm

4.2.1 Adsorption and desorption isotherms

4.2.2 Effect of temperature on isotherms

4.3 Evaluation of moisture sorption hysteresis

4.4 Isotherm modeling

4.5 Evaluation of temperature dependence of GAB parameters

4.6 Evaluation of net isosteric heat of sorption

4.1 Compositional analysis of "thabdi"

Thabdi prepared from buffalo milk was used as a test sample for present study. Chemical analysis carried out by following standard procedures. The composition of *thabdi* determined by standard methods is presented in Table 4.1.

Table 4.1. Composition of *thabdi* prepared from buffalo milk

Parameter	% by weight
Moisture (w.b.)	10.49
Fat	26.68
Protein	13.54
Lactose	18.14
Sucrose	29.04
Ash	3.21
Titratable Acidity % (LA)	0.36

4.2 Sorption isotherm

A deep knowledge of sorption isotherm is very essential in appraising the shelf life of the product in the packaging material and prediction of drying time in food stuffs (King, 1968). The need for reliable sorption data has always arisen in the formulation of shelf stable foods. Besides this, the isotherm equation is also useful for evaluation of the thermodynamic function of water sorbed in food.

4.2.1 Adsorption and desorption isotherm

The experimental data for the equilibrium moisture content along with the standard deviations based on triplicate measurement at three different temperatures are presented in Table 4.2 and Table 4.3 respectively:

Moisture sorption isotherm of *thabdi* prepared from buffalo milk at 15, 25 and 35^{o}C were estimated. Adsorption and desorption isotherms of *thabdi* drawn by joining experimental data which are measured at above temperature are represented in fig. 4.1 to 4.6. All sorption isotherms demonstrate an increase in equilibrium moisture content with increasing water activity. In all the isotherm figures there was a slow increase up to 0.2 a_w. Then the moisture uptake increased and remained moderate

Table 4.2 Equilibrium moisture content (g/100g solids) of thabi at different temperatures and water activity for adsorption

15˚C			25˚C			35˚C		
a_w	M*	S.D.**	a_w	M*	S.D.**	a_w	M*	S.D.**
0.113	5.91	0.04	0.113	5.02	0.11	0.1125	4.92	0.09
0.333	8.98	0.21	0.328	7.56	0.71	0.32	6.44	0.52
0.431	10.01	0.25	0.432	8.64	0.48	0.432	7.74	0.61
0.559	11.6	0.17	0.529	10.02	0.6	0.499	9.65	0.94
0.756	17.54	1.01	0.753	16.21	0.72	0.749	15.68	0.92
0.817	22.04	0.71	0.81	20.84	0.86	0.802	18.34	0.85
0.953	41.64	0.81	0.936	39.79	0.84	0.907	38.94	1.1
0.979	58.64	1.27	0.973	55.23	0.56	0.967	52.94	1.02

M*=mean of N=3 replications, S.D.**= Standard deviation of N=3 replications

up to 0.8 a_w. Then there was a steep rise in the moisture uptake beyond 0.8 a_w (80%relative humidity).

This behavior is manifested in the form of a sigmoid shape curve, thus reflecting a **Type II** isotherm (Brunauer *et al.* 1938), which is typical to most of the foods. All sorption isotherms demonstrate an increase in equilibrium moisture content with increasing water activity. Similar behaviour was observed for desorption isotherms. Isotherms showed that the product adsorbed proportionately more water towards the later part of the curve.

Table 4.3 Equilibrium moisture content (g/100g solids) of thabdi at different temperatures and water activity for desorption

15˚C			25˚C			35˚C		
a_w	M*	S.D.**	a_w	M*	S.D.**	a_w	M*	S.D.**
0.113	6.16	0.38	0.113	5.68	0.68	0.1125	5.11	0.14
0.333	9.64	0.21	0.328	8.47	0.59	0.32	7.26	0.75
0.431	10.98	0.73	0.432	9.25	0.34	0.432	8.42	0.41
0.559	13.04	0.21	0.529	11.36	0.57	0.499	10.43	0.85
0.756	18.86	0.32	0.753	17.54	0.63	0.749	16.71	0.55
0.817	23.18	0.79	0.81	21.84	0.89	0.802	20.58	1.11
0.953	42.34	1.04	0.936	40.21	1.14	0.907	39.47	1.24
0.979	59.14	1.01	0.973	56.61	1.21	0.967	54.71	1.01

M*=mean of N=3 replications, S.D.**= Standard deviation of N=3 replications

Similar types of observations were found by Lin *et al.* (2002) for milk powders, Kumar and Venugopal (1991) for infant foods, Sawhney *et al.* (2010) for dried acid casein from buffalo whole milk, Govardhan (2007) for gulabjamun mix powderand Sawhney *et al.* (1991) for khoa. Prateek (2003) observed the steep rise in EMC at higher water activity in basundi.

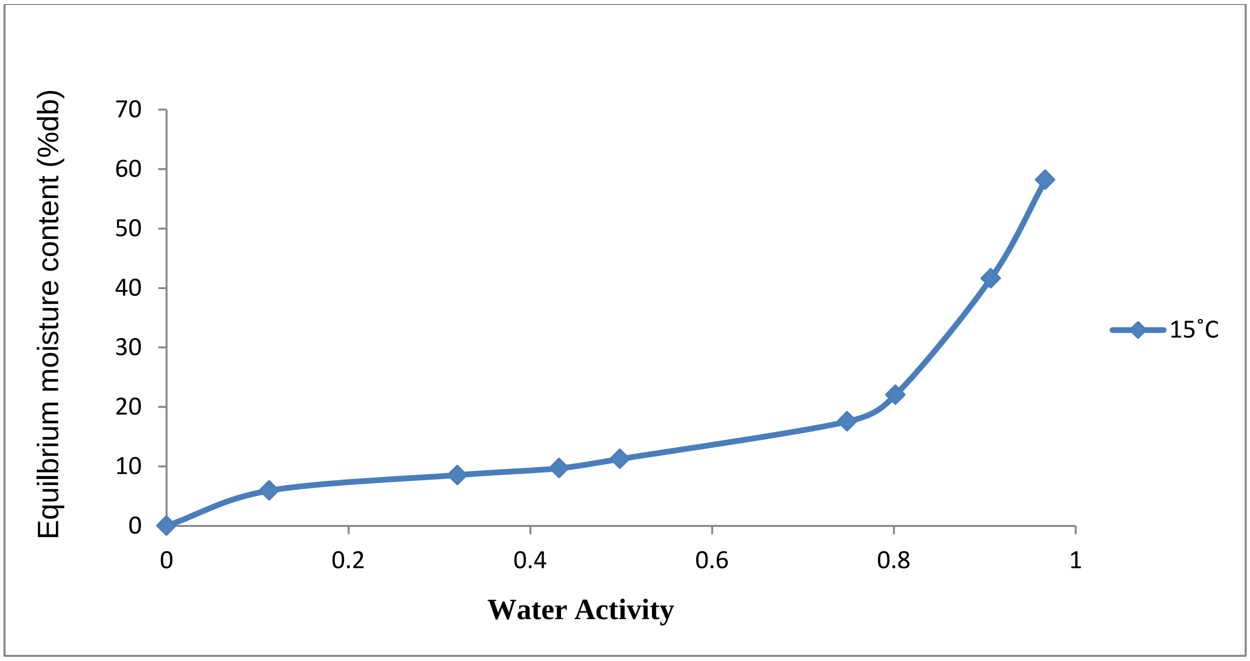

Fig. 4.1. Moisture Adsorption Isotherm of *thabdi* at 15ºC

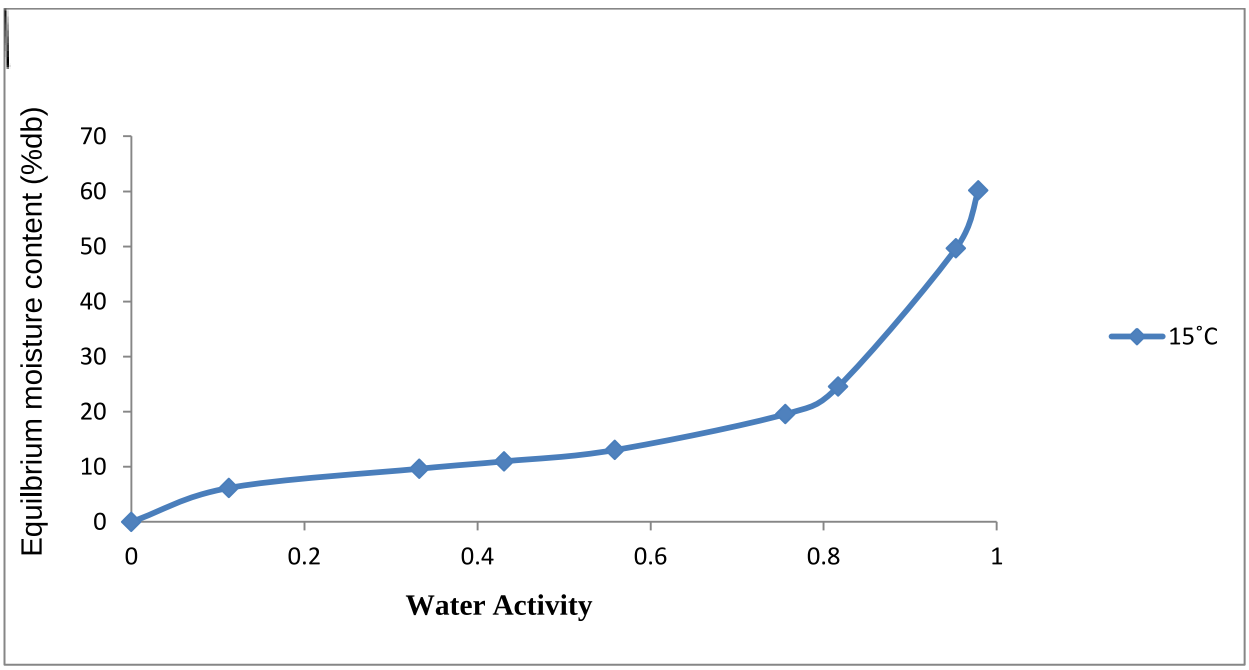

Fig. 4.2. Moisture Desorption Isotherm of *thabdi* at 15ºC

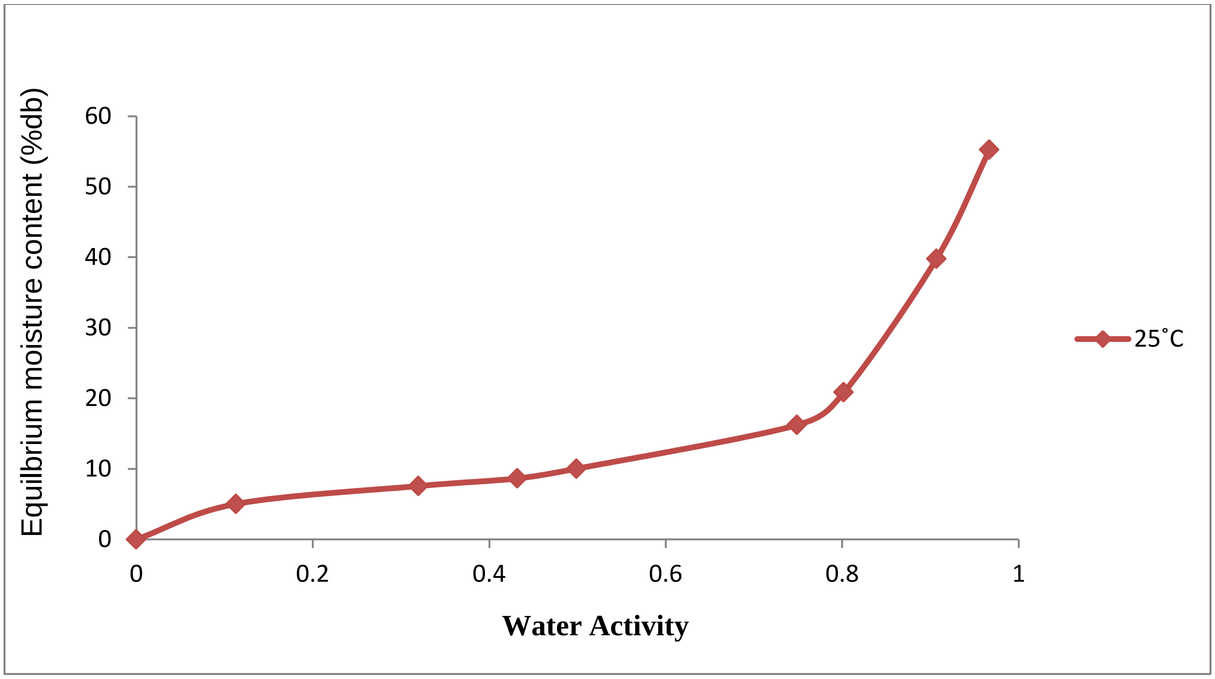

Fig. 4.3. Moisture Adsorption Isotherm of *thabdi* at 25⁰C

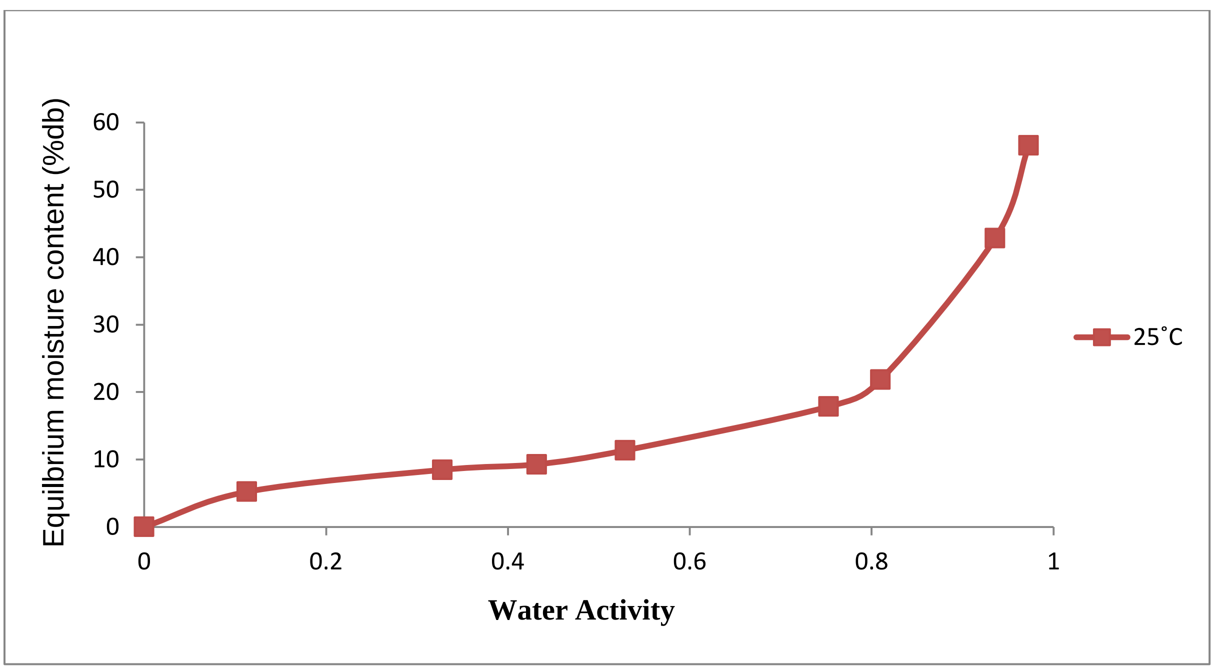

Fig. 4.4. Moisture Desorption Isotherm of *thabdi* at 25⁰C

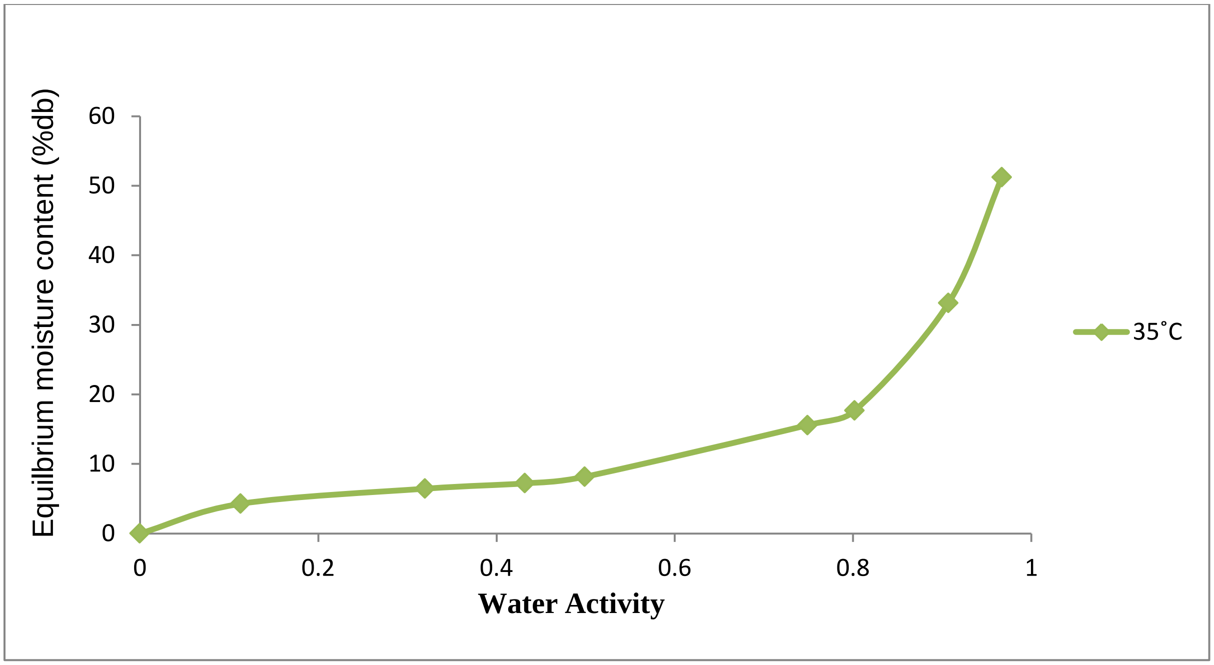

Fig. 4.5. Moisture Adsorption Isotherm of *thabdi* at 35ºC

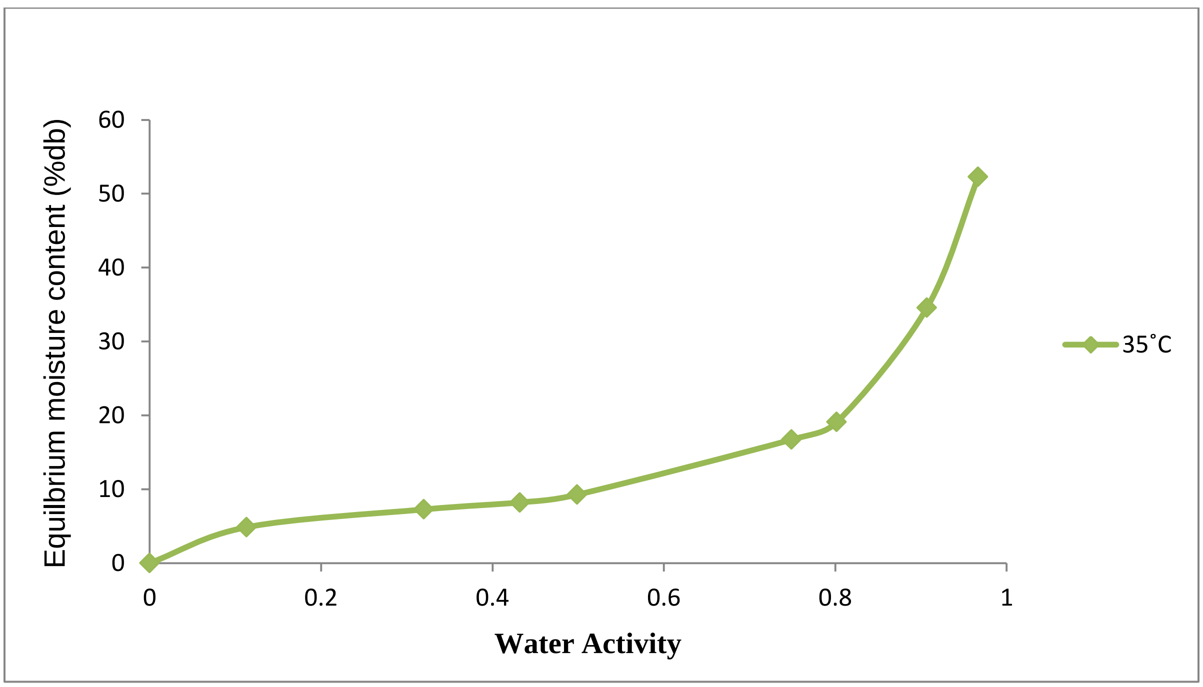

Fig. 4.6. Moisture Desorption Isotherm of *thabdi* at 35ºC

4.2.2 Effect of temperature on isotherm

Water activity is an important control variable in food processing. Understanding the temperature dependence of moisture sorption phenomena in food helps in giving valuable information for characterization of storage and packaging problems.

The effect of temperature on adsorption and desorption isotherm of thabdi are shown in fig 4.7 & 4.8. It may be seen that from 0.2 a_w all the three curves of adsorption distinguishable. In case of desorption it can be seen that all the curves were clearly distinguishable in the water activity range of 0.2 to 0.9. Above 0.9 a_w and below 0.2a_w the curves are superimposing on each other. It was also noted that at a particular water activity equilibrium moisture content was lower at higher temperature. The equilibrium moisture content is seen to decrease with increase in temperature at the same a_w or a_w increases with increase in temperature at the same equilibrium moisture content. There was a consistent shift to the right in the adsorption and desorption isotherm at all the three temperatures.

The effect of temperature on the sorption isotherm is of great importance because the foods are exposed to a range of temperatures during storage and processing and water activity changes with temperature. Temperature affects the mobility of water molecules and dynamic equilibrium between vapour and adsorbed phase (Al-Muhtaseb *et al*., 2004).

The analysis of variance (ANOVA) presented in Table 4.2 was carried out to check the effect of temperature and water activity on the equilibrium moisture content. The null hypothesis was set as there is no significant effect of temperature and water activity on the equilibrium moisture content. However the results obtained revealed that the effect of temperature on moisture content was statistically significant ($P>0.05$) over the temperature range of 15 – 35^{o}C. Thus it can be said that there is a significant effect of temperature and water activity on the equilibrium moisture content. Foster *et al*. (2005) has observed no obvious temperature

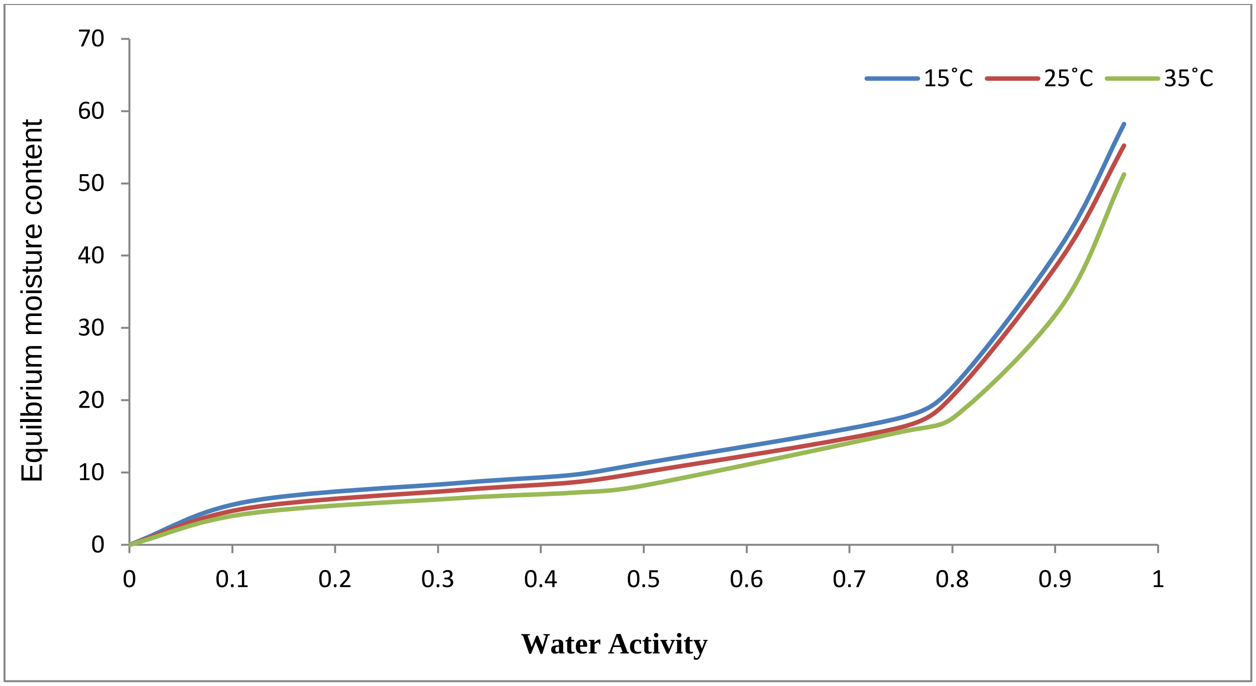

Fig. 4.7 Moisture Adsorption Isotherm of *thabdi* at 15^{0}C, 25^{0}C and 35^{0}C

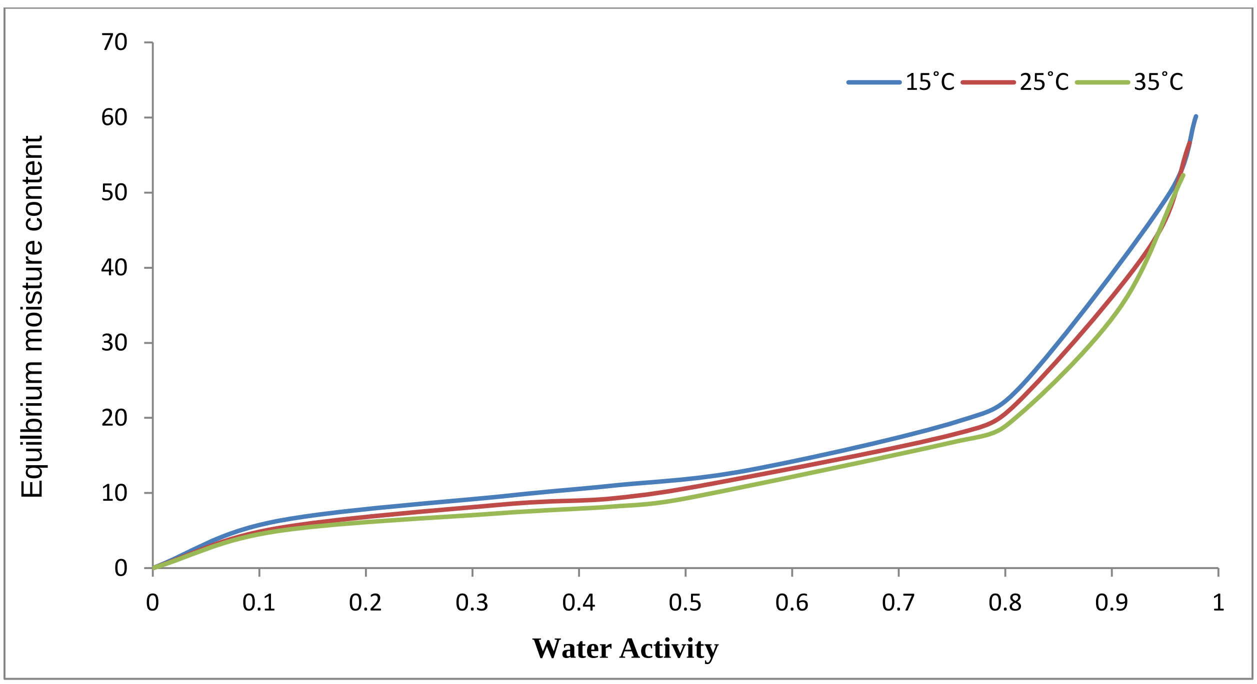

Fig. 4.8 Moisture Desorption Isotherm of *thabdi* at 15^{0}C, 25^{0}C and 35^{0}C

Table 4.4 ANOVA results for adsorption and desorption

ANOVA Adsorption						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Water Activity	6526.689	7	932.3841	494.8952	1.15E-15	2.764199
Temperature	61.85976	2	30.92988	16.41711	0.000213	3.738892
Error	26.37604	14	1.884003			
Total	**6614.925**	**23**				

ANOVA Desorption						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Water Activity	7022.109	7	1003.158	196.6494	6.94E-13	2.764199
Temperature	107.5553	2	53.77765	10.54205	0.001611	3.738892
Error	71.41756	14	5.101254			
Total	**7201.081**	**23**				

dependence in isotherm of high miceller casein powder measured between 4-37^oC but found the isotherm at 50^oC to be significantly lower at water activities above 0.2.

4.3 Evaluation of moisture sorption hysteresis

The moisture sorption hysteresis of *thabdi* prepared from buffalo milk at 15, 25 & 35ºC shown in fig 4.9 to 4.11. The hysteresis effect exhibited by *thabdi* shows that the adsorption and desorption isotherms were distinctly apart from each other. The hysteresis loop extends over the entire range of water activity and can be classified as Type - C according to Everett and Whitton classification (Kapsalis, 1981), which begins about 0.9 a_w (upper closing point) and extends over the rest of the isotherm up to 0.12 a_w (lower closing point). The distribution of hysteresis loop relative to water activity showed a marked change at various water activities. The hysteresis effect was moderate in the monolayer moisture content region of thabdi. The hysteresis effect became minimum beyond 0.85 a_w and the adsorption and desorption isotherm of *thabdi* coincides with each other at about 0.91 a_w at 15ºC, 0.9 a_w at 25ºC and 0.88 a_w at 35ºC. Maximum hysteresis was observed between 0.30 to 0.85 a_w range.

Bell and Labuza (2000) reported that foods with high sugar content frequently exhibit this phenomenon and explained that when the water moves out from capillaries of the product, during moisture desorption, the narrow ends of surface pores trapped and held water internally below the water activity where the water should have been released, thus there was greater moisture content at a low range of water activity. During adsorption, the pure water would dissolve solutes, that is lactose, sucrose and salts present in *thabdi* and dissolution of solutes increased the surface tension resulting in lower water activity at given moisture.

A paired t-test and correlation analysis were performed using Excel to compare moisture content sorbed by the samples at different temperatures during the adsorption and desorption. Table 4.3 shows paired t-test results with $t_{0.05}$ = 2.8 at 15ºC, $t_{0.05}$ = 4.2 at 25ºC, and $t_{0.05}$ = 10.5 at 35ºC. The null hypothesis was considered as there is no significant difference between the adsorption and desorption. But the t-test carried out at all the three temperatures were found to be statistically significant ($P>0.05$). Thus it was concluded that there is a significant difference between desorption and adsorption in the hysteresis loop. Further, high correlation ($\gamma = 0.998$) between adsorption and desorption data revealed significant association between them.

The hysteresis loop was evaluated in terms of relative hysteresis units as described by Wolf et al. 1972. For this purpose the adsorption values were subtracted from the respective desorption values at a given water activity intervals of 0.1 and the resulting difference was plotted versus the corresponding water activity. Figure 4.12 shows the hysteresis value of thabdi at different temperatures. The graphical integration of area under this curve gave the hysteresis units. The total hysteresis in *thabdi* was 1.34 units at 15^{o}C. The magnitude of hysteresis was smaller at higher temperatures. Yan *et al*. (2008) attributed this phenomenon to the increased elasticity of capillary walls and greater capability of forming hydrogen bond between protein/carbohydrate and water. In *thabdi* from buffalo milk, the effect of increasing the isotherm temperature was found decreasing the total hysteresis from 1.24 units at 15^{o}C to 1.01 at 25^{o}C and 0.86 at 35^{o}C. It also resulted in limiting the span of the loop along the isotherm.

The hysteresis amplitude for a given water activity is characterized by relative water content difference between desorption and adsorption. The hysteresis amplitude ratio varied throughout the water activity range of 0.12 to 0.9 at all the temperatures. However, the maximum value for this ratio in thabdi was 0.383 at 15^{o}C. It reduced with increase in temperature to 0.264 at 25^{o}C and 0.213 at 35^{o}C. In most foods, the sorption capacity decreases with increasing temperatures because of negative excess heat of sorption (Bizot *et al*., 1985). The results obtained on thabdi are in agreement to this.

Total hysteresis energy was determined employing the equation 3.23. The Everett and Whitton plots of sorption data on *thabdi* at 15, 25 and 35^{o}C are shown in the Figure 4.13. In this figure the x-axis has been expressed, for the convenience in interpretations, on a moisture content basis, where as for calculating the total energy, the number of mole of water has been used. The Everett and Whitton plot indicate that the greater contribution to hysteresis energy is made in the moisture content range 6 to 10% (d.b.). The energy of hysteresis was not uniform over the whole water activity range, but varied with the moisture content.

The hysteresis energy increased in the beginning with the moisture content and there after decreased abruptly and remained almost uniform. The total energy of hysteresis decreased with increase in temperature; it was 48.75 kJ/kg of water at 15ºC, 37.64 kJ/kg of water at 25ºC and 31.43 kJ/kg of water at 35ºC. The effect of temperature was thus found to reduce hysteresis energy. The plot also indicates that the greater contribution of this energy is made over the lower moisture range.

Pagire, 2011, evaluated the hysteresis of peda at the 15, 25 and 35˚C. The hysteresis energy of peda was 67.72kJ/kg water at 15ºC which reduced to 32.25kJ/kg water at 35ºC. The hystereisis energy of thabdi also showed similar results.

The use of quantitative index of quality for thabdi appears as a promising possibility. The hysteresis characteristics in thabdi may then serve to evaluate the shelf life of product under varying storage conditions and design of suitable packaging system.

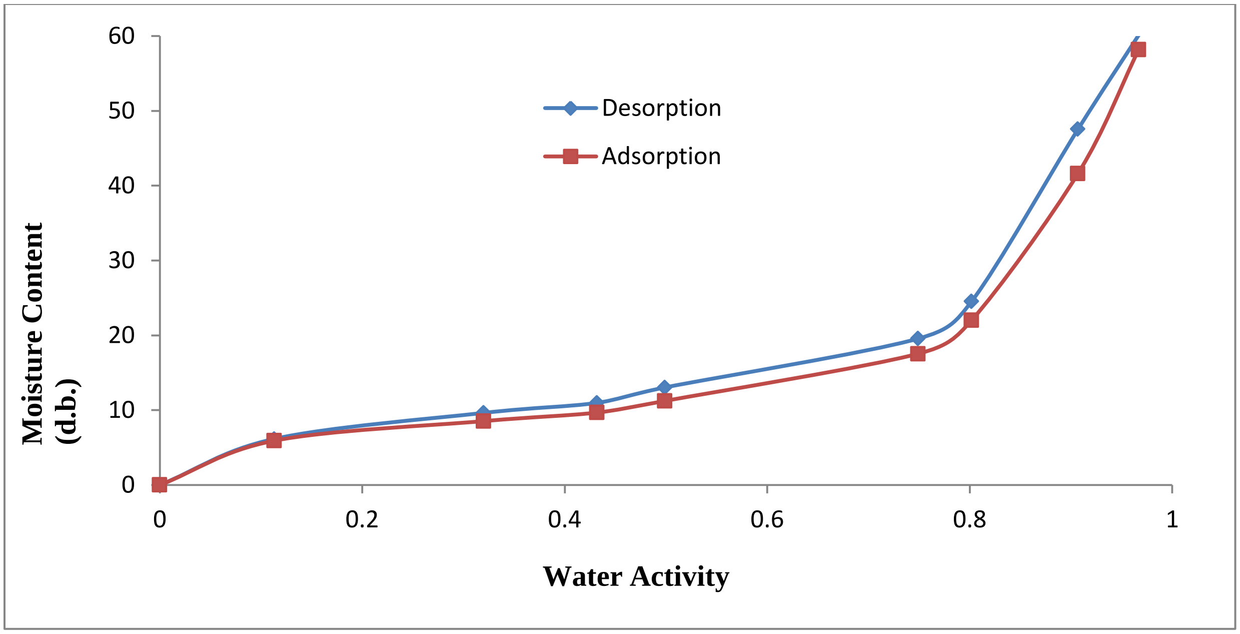

Fig. 4.9. Moisture sorption hystresis of *thabdi* at 15^{o}C

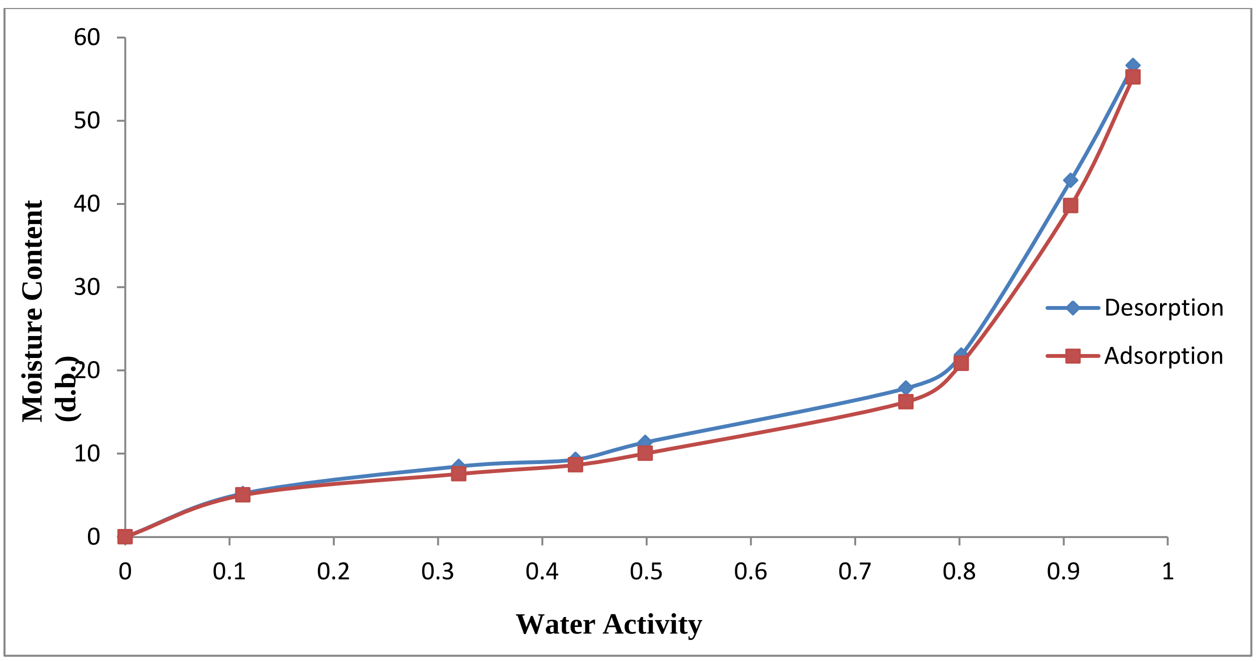

Fig. 4.10. Moisture sorption hystresis of *thabdi* at 25^{o}C

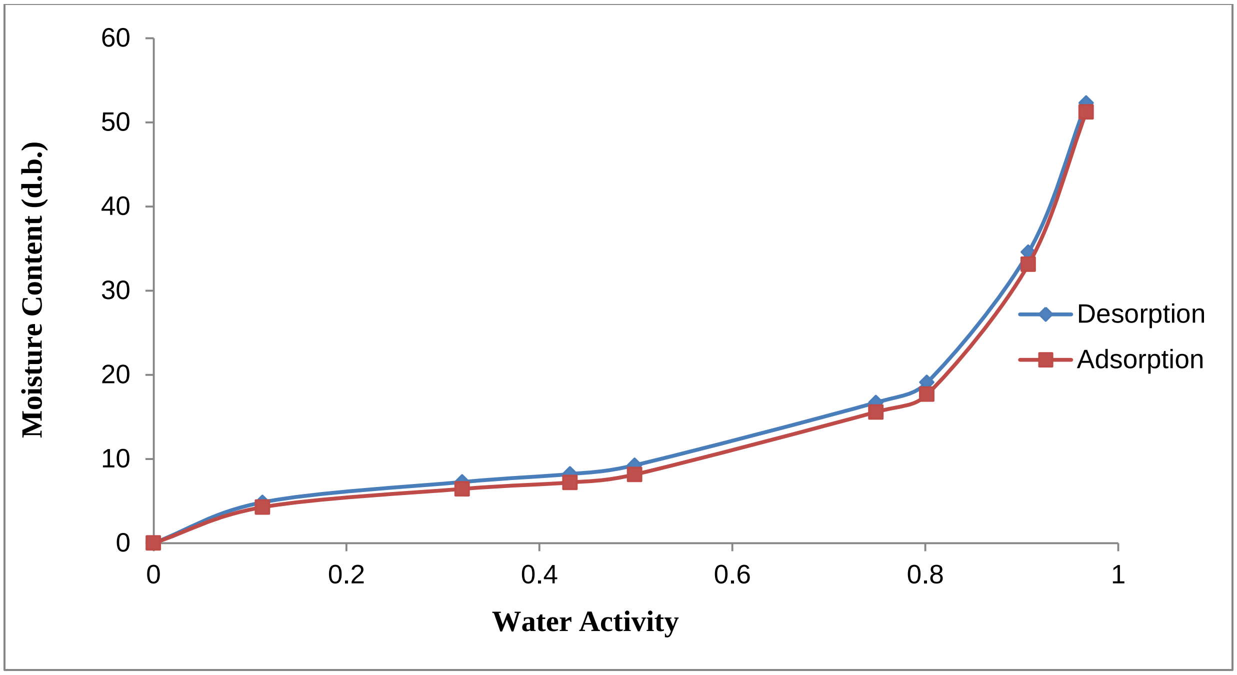

Fig. 4.11. Moisture sorption hystresis of *thabdi* at 35ºC

Table: 4.5 Paired t-test for two sample means at different temperatures

Temperature	Adsorption	Desorption	t- Stat
15˚C	24.21875	21.85124	2.805
25˚C	21.685	20.41375	4.219
35˚C	19.03375	17.9625	10.539

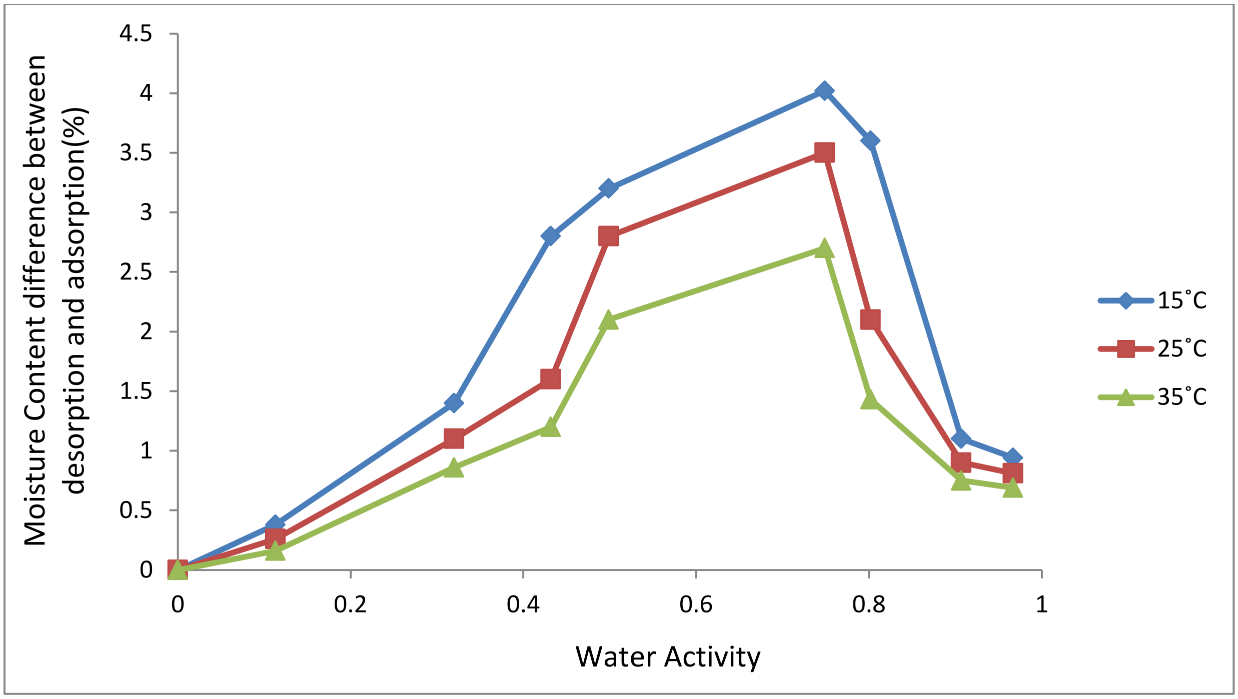

Fig. 4.12.Effect of temperature on derived hystresis of *thabdi*

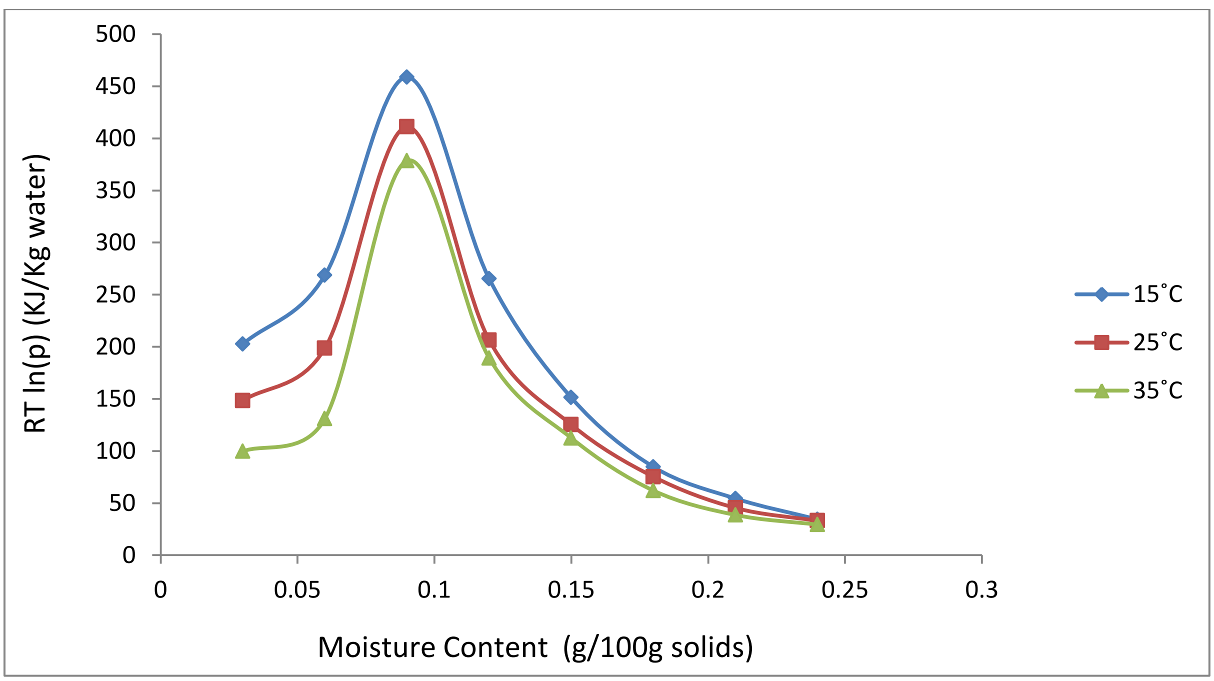

Fig.4.13.Everett and Whitton plot for moisture sorpion data on *thabdi* at different temperature

4.4 Modeling of Isotherm

The experimental data on moisture sorption was fitted to five different two and three parameter models using Eq. 3.9 to 3.13. Estimated parameters and root mean square per cent error (% RMS) for selected models of isotherm in the water activity and temperature ranges studied are presented in Table 4.6 for adsorption isotherm and Table 4.8 for desorption isotherm. The lower is the value of % RMS for predicted and experimental values; the better would be the goodness of fit. A good description of the isotherm is considered, on average, to be smaller than % RMS of 7.0 when a model is applied (Palou *et al*., 1997).

Examination of the results in above tables indicted that the GAB model best described the experimental adsorption and desorption data for thabdi throughout the entire range of water activity. In the present study, at 15, 25 and 35ºC the GAB predicted the adsorption and desorption isotherm between 3.07 and 5.59% RMS. This was followed by Halsey with % RMS between 5.91 and 8.21. Since Modified Mizrahi equation was not defined for the whole range of water activity (0.11-0.97), this study resulted in the GAB as best fitted equation for both adsorption and desorption isotherms. GAB equation was fitted precisely up to 0.90 a_w as well as it provide the better evaluation of amount of water tightly bound by primary adsorption sites.

The values of monolayer moisture content 'W_m' and GAB constants C and K calculated for *thabdi* at three temperatures 15, 25 and 35^oC are presented in Table 4.4 for adsorption and Table 4.6. for desorption. The results show that the adsorbed monolayer moisture content of thabdi decreased from 5.82 at 15^oC to 4.44 g/100g solids at 35^oC. Similarly, the desorption monolayer decreased from 6.61 at 15^oC to 5.04 g/100g solids at 35^oC. The temperature dependence of monolayer moisture has been linked to a reduction in sorption active sites as a result of physicochemical changes induced by temperature. This behavior has also been reported for many other food systems (Iglesias and Chirife, 1976).

Table 4.6 Estimated parameters and root mean square percent error for selected models of adsorption isotherm at different temperatures for thabdi

Equation	Temperature	Constants			%RMS
		A	b	c	
Halsey	15˚C	14062.03	1.7410	-	7.4355
Oswin		12.3227	0.4493	-	11.8783
Caurie		-4.2408	7.3943	-	16.2127
Modified Mizrahi		-4.5013	-6.9117	9.2133	13.7639
GAB		-0.1591	0.1704	0.0007	5.9556
Halsey	25˚C	9600.2461	1.6600	-	8.2117
Oswin		11.0614	0.4722	-	11.7449
Caurie		-4.2889	8.7218	-	13.7306
Modified Mizrahi		-3.630	-7.2451	8.7573	14.6549
GAB		-0.1757	0.1845	0.0028	5.6817
Halsey	35˚C	6632.966	1.6104	-	6.5794
Oswin		9.4711	0.6842	-	11.5644
Caurie		-4.3082	10.43362	-	14.4632
Modified Mizrahi		-3.0818	-6.1123	7.2292	13.0997
GAB		-0.2096	0.2176	0.0038	3.3571

Table 4.7 Parameter values for GAB model to describe the adsorption isotherm of *thabdi* at different temperature

Temperature	GAB Parameters		
	$W_\circ$	C	k
15˚C	5.82174	251.666	0.92993
25˚C	5.26516	70.3887	0.93828
35˚C	4.44466	61.2609	0.94723

Table 4.8 Estimated parameters and root mean square percent error for selected models of desorption isotherm at different temperatures for thabdi

Equation	Temperature	Constants			%RMS
		a	b	c	
Halsey	15˚C	29468.34	1.9957	-	7.6644
Oswin		11.9280	0.4061	-	6.7841
Caurie		-4.2360	6.8527	-	12.7100
Modified Mizrahi		-4.3356	-10.7133	13.6451	14.5162
GAB		-0.1349	0.1472	0.0022	4.5944
Halsey	25˚C	14718.84	1.8043	-	6.7651
Oswin		12.9617	0.4803	-	6.8019
Caurie		-4.2818	8.1614	-	11.1467
Modified Mizrahi		-3.6052	-9.7299	11.6975	12.1345
GAB		-0.1527	0.1628	0.0040	4.2509
Halsey	35˚C	9486.652	1.6913	-	5.9185
Oswin		10.5061	0.4634	-	10.2394
Caurie		-4.2760	9.0297	-	14.2061
Modified Mizrahi		-3.5231	-6.9262	8.5401	12.5706
GAB		-0.1826	0.1925	0.0030	3.0706

Table 4.9 Parameter values for GAB model to describe the desorption isotherm of *thabdi* at different temperature

Temperature	GAB Parameters		
	$W_{\circ}$	C	K
15˚C	6.6119	75.8452	0.90384
25˚C	5.8751	45.6582	0.91637
35˚C	5.04327	69.7714	0.93417

From table 4.7 and 4.9, $W_{\circ}$ is the moisture content on dry basis which is equivalent to monomolecular layer of water, C is Guggenheim constant at constant temperature and K is parameter which improves the fit to a wider range of moisture content than the BET equation. From the tables it is very well observed that there is a decrease in monolayer moisture content as the temperature increases which is found in other food systems too.

4.5 Evaluation of temperature dependence of GAB parameter

The variation in water activity at any given temperature could be predicted by incorporating temperature term into sorption equations. Equations have been developed to correlate the GAB constants with temperature employing the isotherm data at 15, 25 and 35^{o}C. Eq. 3.20 to 3.22 were used to determine W'm, C' and k' and the corresponding exponents in these equations by least square analysis for adsorption and desorption in thabdi prepared from buffalo whole milk.

For Adsorption

$$W_m(T)_a = 1.0213.exp(2.8614 \times 10^3 / RT) \quad \text{...... (4.1)}$$

$$C(T)_a = 0.0173.exp(17.918 \times 10^3 / RT) \quad \text{....... (4.2)}$$

$$K(T)_a = 0.0123 .exp(9.2611 \times 10^3 / RT) \quad \text{....... (4.3)}$$

For Desorption

$$W_m(T)_d = 1.4261.exp(3.6170 \times 10^3 / RT) \quad \text{....... (4.4)}$$

$$C(T)_d = 0.0215.exp(18.618 \times 10^3 / RT) \quad \text{....... (4.5)}$$

$$K(T)_d = 0.0201 .exp(8.4551 \times 10^3 / RT) \quad \text{....... (4.6)}$$

The Equations 4.1 to 4.6 together with equation of GAB model (Eq. 3.12) can now be used to calculate the equilibrium water content of the *thabdi* at any given water activity and temperature for adsorption as well as desorption isotherm. These equations could gainfully be used in shelf life simulation and storage and dehydration of the *thabdi*.

4.6 Evaluation of net isosteric heat of sorption

Study of sorption isotherms at least at two different temperatures provides thermodynamic data on isosteric heat of sorption. The isosteric heat of sorption varies with the amount of water adsorbed by the substrate.

Labuza *et al*. (1985) and Weisser (1985) showed that the net isosteric heat of sorption-desorption could be predicted by generalized equation of Clausius-Clapeyron equation. The isosteric heat of adsorption and desorption for thabdi was calculated by applying equation (Eq. 3.18) to the moisture sorption data as expressed by the GAB model that best described the isotherms. The isosteric heat has a strong dependence on moisture content, with the energy required for sorption (in excess of latent heat) increasing at low moisture content. By plotting $\ln(a_w)$v/s inverse of absolute temperature straight line called isosters at particular moisture content were obtained. The sorption isosters of *thabdi* at different moisture content for adsorption and desorption were shown in Fig. 4.14 & 4.15. Net isosteric heat of sorption was calculated by taking slope of each isosters. It was found that net isosteric heat of sorption decreases with increasing moisture content. The isosteric heat of sorption as a function of moisture content is presented in Fig. 4.16 for adsorption and desorption for *thabdi*. Isosteric heat of adsorption was found to decrease with increase in moisture content and the trend seemed to become asymptotic as the moisture content of above 10.49 % dry basis was approached. The maximum isosteric heat of adsorption obtained was 58.11 kJ/mol for desorption and 39.06kJ/mol for adsorption of *thabdi*. The maximum enthalpy value indicates the covering of the strongest binding sites and the greater water solid interactions in the *thabdi*. Therefore, the water binding in *thabdi* prepared from buffalo milk was found to be weak at moisture content above 15%. Similar trends have been reported for the isosteric heats of several food such as khoa (Sawhney *et al*., 1991), cookies and snacks (Palou *et al*., 1997), potato (McMinn and Magee, 2003), tow mints (Kane *et* *al*., 2008), chhana podo (Jayaraj *et al*., 2006), walnut kernels (Togrul and Arslan, 2006), kheer (Jayendra *et al*., 2005). At low moisture levels, the adsorption is mainly at monomolecular layer where the sorption sites are usually active (Iglesias and Chirife, 1976).

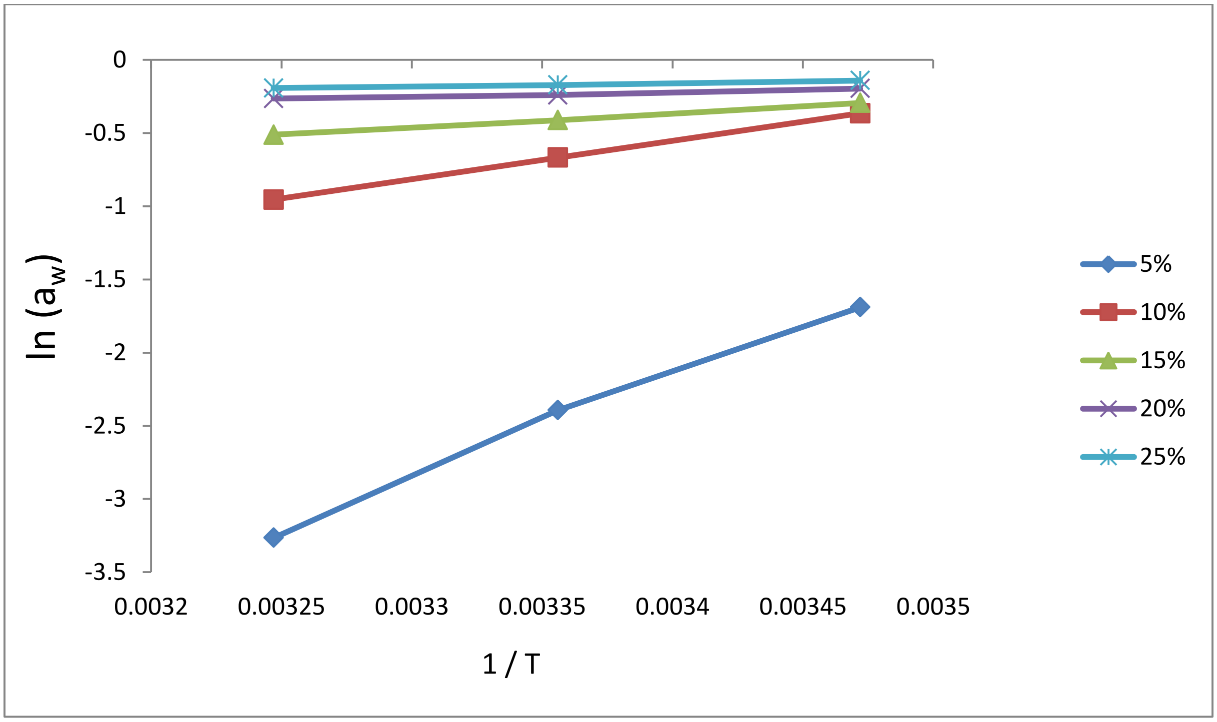

Fig. 4.14 Moisture sorption isosters of adsorption for *Thabdi* at different moisture content

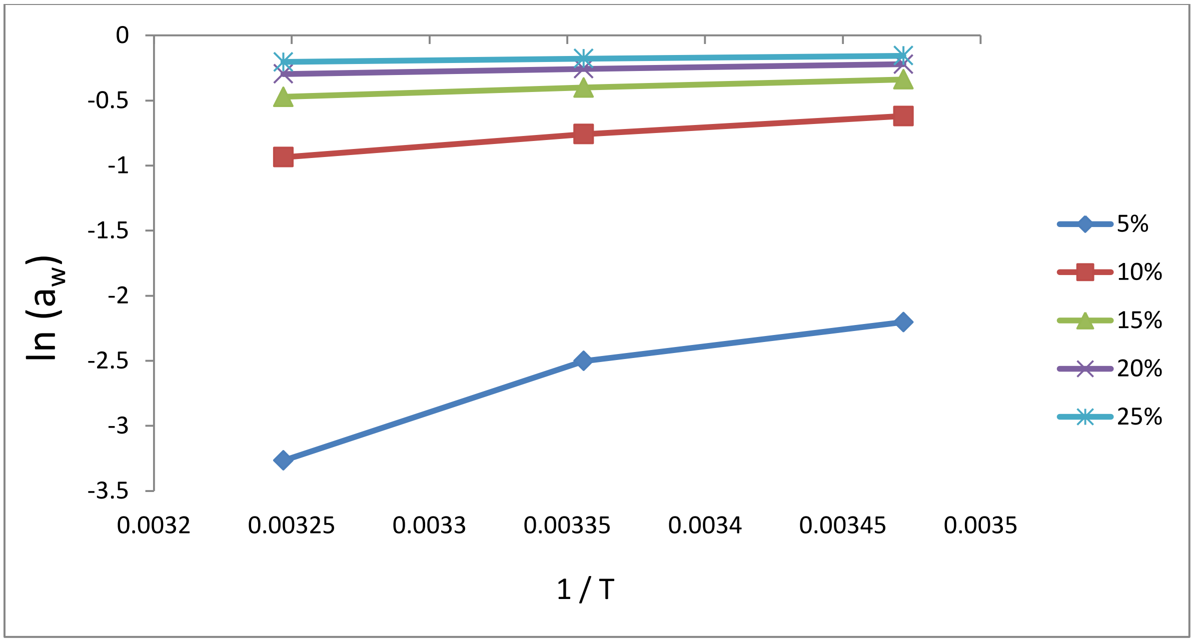

Fig. 4.15 Moisture sorption isosters of desorption for *Thabdi* at different moisture content

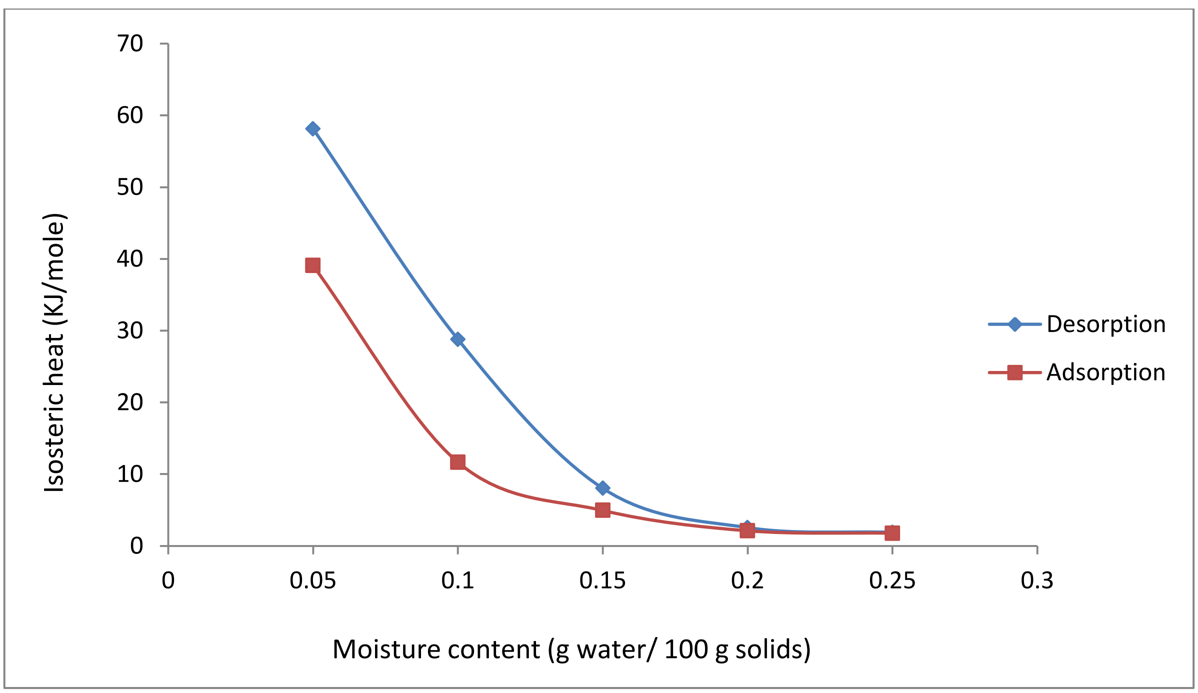

Fig. 4.16 Variation in differential enthalpy (isosteric heat) of adsorption and desorption of thabdi with moisture content.

The isosteric heats of adsorption and desorption were higher than the latent heat of pure water, indicating that the energy of binding between the water molecules and the sorption sites was higher than the energy which holds the water molecules in the liquid phase. All the above figures revealed that the heat required for adsorption process was generally greater than that for the desorption process. The increased energy requirements of the former process are indicative of the more polar sites on the surface of material and hence molecules of lower mobility. As the moisture content increased, the difference between the isosteric heat values for adsorption and desorption processes was observed to decrease. The difference between heats of adsorption and desorption was greater at lower moisture contents, converging as the moisture content increased and practically disappearing above 15% moisture content (d.b.). Benado and Rizvi (1985) reported a similar observation for the sorption behaviour of rice. These changes are probably due to changes in molecular structure during sorption which affects the degree of activation of sorption sites. No relationship exists between the degree of hysteresis and the variation of isosteric heats of sorption (Al-Muhtaseb *et al*., 2004).

The information of isosteric heat may be useful in calculating the cumulative energy requirement for dehydration of thabdi.

CHAPTER – 5

Summary and Conclusions

Thabdi is one of the most popular dairy product found in the Saurashtra region of Gujarat State. *It* is a heat desiccated whole milk product sweetened with added sugar at the time of manufacture. It has brown to dark brown colour with caramelized taste and flavor and has a distinct granular texture which is held together loosely.

The current investigation was carried out in Dairy Engineering Division of NDRI, Karnal. Milk was obtained from Experimental Dairy Plant of NDRI, Karnal, for preparation of *thabdi*.

The sorption isotherms describe the equilibrium relationship between water activity (aw) and moisture content of the food, at constant temperatures and pressures. The understanding and control of a_w contributes to safer food storage conditions in general and forms a basis of much modern food formulations, especially for intermediate moisture foods.

The study have been carried out to develop moisture sorption isotherm of *thabdi* prepared from buffalo milk at 15, 25 and 35ºC by using standard gravimetric method suggested by Wolf *et al.,* (1985). Eight reagent grade salt slurries were chosen (Greenspan, 1977) to maintain different water activities. About 1 gm of *thabdi* sample was equilibrated with the environment of different relative humidity. The desiccators containing samples were placed at 15, 25 and 35ºC to evaluate the influence of temperature on moisture sorption characteristics of *thabdi*. Experimental data were fitted to various models by using least square linear regression method. The model which was having least root mean square error percentage value was selected as best fitted model. GAB showed best fit to the experimental data of *thabdi.*

The net isosteric heat of sorption was calculated by using Clausius-Clapeyron equation. By least square analysis the temperature dependence of GAB parameter were found out. The hysteresis effect was quantified by plotting combined adsorption-desorption isotherm and evaluating hysteresis amplitude, hysteresis units and hysteresis energy. The conclusions derived from this study are as follows:

I. The initial water activity of thabdi at 10.5% moisture content (d.b.) was found to be 0.829 at 25˚C.

II. All sorption isotherm of thabdi prepared from buffalo milk were Sigmoid in shape, showing type II isotherm.

III. It was concluded from the data of the sorption isotherm of *thabdi* that there was a negative temperature effect on equilibrium moisture content at a given water activity and a positive temperature effect on water activity at a given equilibrium moisture content.

IV. Monolayer moisture content was higher in desorption ie. 6.16 g/100 g water at 15˚C at 0.113 water activity and in both adsorption and desorption it decreased with increase in temperature.

V. GAB equation was found to be the best fitted equation for the experimental data of thabdi.

VI. RMS values of GAB equation were found in the range of 3.07% to 5.59%

VII. The hysteresis loop was classified as Type-C according to Everett and Whitton classification, and it extended in the range of 0.1 to 0.9 water activity.

VIII. Maximum hysteresis was found in between the water activity range of 0.3 to 0.85 water activity. The hysteresis effect decreased with increase in the temperature.

IX. With increase in temperature hysteresis unit decreased from 1.34 units at 15˚C to 0.86 units at 35˚C.

X. Hysteresis amplitude ratio reduced from 0.383 at 15˚C to 0.213 at 25˚C.

XI. Total hysteresis energy decreased with increase in temperature. It was 48.75 KJ/kg of water at 15˚C and reduced to 31.43KJ/kg of water at 35˚C.

XII. Maximum isosteric heat obtained for adsorption was 39.06 KJ/mol and for desorption it was 58.11 KJ/mol. This data can be used for the design of equipment for manufacturing thabdi.

CHAPTER – 6

Bibliography

Bilbliography

Acott, K.M. and Labuza, T.P. 1975. Microbial growth response to water sorption preparation. *Journal of Food Technology.* 10: 603-611.

Al-Muhtaseb, A. H., McMinn, W. A. M., and Magee, T. R. A. 2004. Water sorption isotherms of starch powders Part 2: Thermodynamic characteristics. Journal of Food Engineering, 62, 135–142.

Aviara, N.A., and Ajibola. 2002. Thermodynamics of moisture sorption in melon seed and cassava. *Journal of Food Engineering.* 55: 107-113.

Bell, L.N., and Labuza, T.P. 2000. *Moisture Sorption, Practical Aspects of Isotherms Measurements and Use.* St. Paul, MN: AACC International Publishing.

Berlin, E. 1981 Hydration of milk proteins. In Water activity: Influence on food quality. Rockand, L.B. and Stewart, G.F. (Eds) Academic Press, Inc. New York U.S.A.

Berlin, E., Anderson, B.A. and Pallanch, M.J. 1968. Water vapour sorption properties of various dried milks and wheys. *Journal of Dairy Science.* 51(9): 1339-1344.

Bizot, H., Buleon, A., Mouhous-Riou, N. and Multon, J.L. 1985. Some facts concerning water vapour sorption hysteresis on potato starch. In D. Simota and J.L. Moulton (Eds.) *Properties of Water in Foods.* The Netherlands: Matinus Nijhoff Publishers, Dordrecht, p.83.

Boquet, R., Chirife, J. and Iglesias H. A. 1978. Equation for fitting water sorption isotherms of foods. Part-Ill. Evaluation of Various three parameters models. *Journal of Food Technology.* 14: 527-534.

Brunauer, S., Emmet, P.H. and Teller, E. 1938. Adsorption of gases in ultimolecular layer. *Journal of American Chemical Society.* 60: 309-319.

Caurie, M. 1970. A new model equation for predicting safe storage moisture level for optimum stability of dehydrated foods. Journal of Food Technology. 5: 301-307.

Caurie, M. 1981. Derivation of full range moisture sorption isotherms. In L.B. Rockland and G. F. Stewert (Eds.). Water Activity. Influences on Food Quality. Academic Press, New York, p.63.

Fasina, 0., Sokhansanj, S. and Tyler, R. 1997. Thermodynamics of moisture sorption in alfalfa pellets. *Drying Technology,* 15: 1553-1570.

Foster, K.D., Bronlund, J.E. and Paterson, A.H.J. 2005. The prediction of moisture sorption isotherm for dairy powders. *Journal of Food Engineering.* 15: 411-418.

Govardhan. 2006. Evaluation of sorption isotherm parameters of Gulabjamun mix powder. M.Tech Thesis. National Dairy Research Institute, Karnal, Haryana.

Govardhan. 2006. Evaluation of sorption isotherm parameters of Gulabjamun mix powder. M.Tech Thesis. National Dairy Research Institute, Karnal, Haryana.

Greenspan, L. 1977. Humidity fixed points of binary saturated aqueous solutions. *Journal of Research, National Bureau of Standards A: Physics and Chemistry.* 81: 89-96.

Heiss, Labuza, T.P. 1968, Sorption phenomena in foods. Journal of food technology. 22: 15-24.

Heldman, D.R., Hall, C.W. and Hedrick, T.l. 1965. Vapor equilibrium relationships of dry milk. *Journal of Dairy Science.* 48: 845.

Iglesias, H. A. and Chirife, J. 1976a. Prediction of effect of temperature on water sorption isotherm of food material. *Journal of Food Technology.* 11: 109-116.

Iglesias, H.A. and Chirfe, J. 1976b. Equilibrium moisture contents of air dried beef, dependence on temperature. *Journal of Food Technology.* 11: 565-573.

Iglesias, H.A., Chirife, J., and Viollaz, P. 1976. Thermodynamics of water vapour sorption by sugar beet root. *Journal of Food Technology.* 11: 91-101.

Jayaraj Rao, K., Amla Dhas Heatwin, Emrald, Magdaline E.E. F., Ghosh, Bikash B., Balasubramanyam, B.V. and Kulkarni, S. 2006. Moisture sorption characteristics of chhana podo at 5oC and 35oC*. J. of Food Engineering*. 76: 453-459.

Johnston, K.A., Duckworth, R.B. (1985). The influence of soluble components on water sorption hysteresis. In D. Simmota , & J.L. Moluton (Eds.), Properties of water in foods (pp. 83-93). Dordrecht, The Netherlands: Matinus Nijhoff Publishers.

Kapsalis, J.G. 1973. Moisture and food characteristics activities report. Research and development associates for military food and packaging.

Kapsalis, J.G. 1981. Moisture sorption hysteresis. L.B. Rockland and G.F. Stewart (Eds.) In *Water activity: Influence on Food Quality*. New York: Academic Press, p.43.

Kapsalis, J.G. 1987. Influence of hysteresis and temperature on moisture sorption isotherm. In water activity: Theory and application to food. By Rockland, L.B. and Beuchat, L.R., (Eds.), Marcel Dekker, Inc. New York, USA. pp.173-214.

Karle, M. and Labuza, T.P. 1968. Non- enzymatic browning in model systems containing sucrose. *Journal of Agriculture and Food Chemistry,* 16: 717.

King, C.J. 1968. Rates of moisture adsorption and desorption in porous dried food stuffs. *Food Technol.* 22:509

Komal. P. 2010. Characterization of thabdi from Saurashtra region of Gujarat. M.Tech thesis. Anand Agricultural University.

Krupa. H. 2011. Standardization of procedure for manufacturing of thabdi. M. Tech thesis, Anand Agricultural University.

Kumar, K.R. and Venugopal, J.S. 1991. Moisture sorption behaviour of Infant milk food formulations. *Indian Journal of Dairy Science.* 44: 632-638.

Kuntz., and Kauzman, W. 1974. Hydration of proteins and polypeptides- Review, Adv. Protein chem. 28: 239-245.

Labuza, 1980. Influence of water activity on food product stability. Journal *of Food Technology*, v. 34(4) p. 36-41, 59.

Labuza, T.P. 1968. Sorption phenomena in foods. *Journal of Food Technology.* 22: 15-24.

Labuza, T.P. 1984. Moisture sorption: Practical aspects of isotherm Measurement and use. American Association of Cereal Chemists, St. Paul, Minnesota, 8-21.

Labuza, T.P., Lomauro, C.J. and Baskshi. A.S. 1985. Evaluation of food moisture sorption isotherm Equations part I. Fruit, vegetable and Meat products. *Lebensmittel- Wissenchaft Technology.* 18: 111-117.

Mazza, G. and Jayas, D.S. 1991. Equilibrium moisture characteristics of sunflower seed, hulls and kernels. *Transactions of the ASAE.* 34: 534-538.

Mcalughlin, C.P. and Magee, T.R.A. 1998. The determination of sorption isotherm and isosteric heats of sorption for potatoes. *Journal of Food Engineerin,* 35: 267-280.

Muhtaseb, A.H., McMinn, W.A.M. and Magee, T.R.A. 2004. Water sorption isotherms of starch powders Part 1: Mathematical description of experimental data. *Journal of Food Engineering.* 61: 297-307.

Okos, M.R., Narsimhan, G., Singh, R.K. and Weitnauer, A.C. 1992. Food dehydration. In D. R. Heldman and D. B. Lund (Eds.). *Handbook of Food Engineering.* New York: Marcel Dekker. p.437.

Oswin, C.R., 1946. The kinetics of package life. Ill. Isotherm. *Journal of Society Chemica/Industry.,* 65: 419-421.

Pagire. S. 2011, Moisture sorption characteristics of peda. M.Tech thesis, NDRI.

Palou, E., Lopez, M.A. and Argaiz, A. 1997. Effect of temperature on the moisture sorption isotherms of some cookies and corn snacks. *Journal of Food Engineering.* 31: 85-93.

Prateek. 2003. Moisture sorption characteristics of ready to use basundi mix. M.Tech Thesis, National Dairy Research Institute, Karnal, Haryana.

Rahman, M.S. and Labuza, T.P. 1999. Water activity and food preservation. In M.S. Rahman (Ed.). Handbook of food preservation. pp. 339-382. New York: Marcel Dekker.

Ramesh, M.N. 2003. Moisture transfer properties of cooked rice during drying. *Lebensmittel-Wissenschaft und Technologie.* 36: 245-255.

Rao. K, Dhas. H. 2004. Moisture sorption characteristics of channa podo. *Journal of Jood Engineering.* 76,2006, 453-459.

Rizvi, S. S. H. 2006 Thermodynamic properties of foods in dehydration. In: Rao, M. A., Rizvi, S. S. H. and Dutta, A K. (Eds). Engineering properties of foods, p. 239- 271. Marcel Dekker, New York.

Ruegg, M. 1985. Water in dairy products related to quality, with special reference to cheese. In D. Simato and J. L. Multon (Eds.). *Properties of Water in Foods.* Dordrecht: Martinus Nijhoff, p.603.

Sahu. D. 2005. Evaluation of sorption isotherm parameters of skim milk powder. M.Tech Thesis. National Dairy Research Institute, Karnal, Haryana.

Sawhney I.K., Cheryan M, 1989, Moisture sorption characteristics of heat desiccated whole milk product (khoa). Lebensm Wiss u Technol 21: 239-241

Sawhney I.K., Patil GR, Bikram Kumar (1991). Studies on water activity modification in heat concentrated whole milk product (khoa). Lebensm Wiss u Technol 21: 239-241.

Sawhney, I.K., Bikram Kumar., Agrawala, S.P. and Patel, A.A. 2000. Evaluation of moisture sorption hysteresis in khoa. *Indian Journal of Dairy Science.* 53(3): 184-189.

Sawhney, I.K., Sarkar, B.C. and Patil, G.R. 2010. Moisture sorption characteristics of dried acid casein from buffalo whole milk. *Journal of Food Science and Technology.* 44: 502-510

Scott. 1957. Water relation of food spoilage microorganisms. *Advances in Food Research.,* 7: 84-127.

Togrul, H. and Arslan, N. 2007. Moisture sorption isotherm and thermodynamic properties of Walnut kernels. Journal of Stored Products Research, 43: 252-264.

Van den Berg, C., and Bruin, S. 1981. Water activityand its estimation in food systems: Theoretical aspects. In L. B. Rockland, & G. F. Stewert (Eds.), Water activity: Influences on food quality (pp. 1–62). New York: Academic Press.

Weisser, F. 1985. Influence of temperature on sorption equilibria. In: Simator, D., Multon, J.L. (Eds.), Properties of Water in Foods. Martinus Nijhoff, Dordrecht, pp.95.

Wolf, M., Waliker, J.E. and Kapsalis, J.G. 1972. Water vapour sorption hysteresis in dehydrated foods. *Journal of Agricultural and Food Chemistry.* 20: 1073-1077.

Wolf, W., Spiess, W.E.L., and Jung, G. 1985. Standardization of isotherm measurements (COST-project 90 and 90 BIS). In D. Simatos, & J. L. Multon (Eds.), Properties of water in foods (pp. 661-677). Dordrecht: Martinus Nihoff Publishers.

Wolf, W., Spiess, W.E.L., and Jung, G. 1985. Standardization of isotherm measurements (COST-project 90 and 90 BIS). In D. Simatos, & J. L.

Multon (Eds.), Properties of water in foods (pp. 661-677). Dordrecht: Martinus Nihoff Publishers.