MOISTURE SORPTION CHARACTERISTICS OF PEDA FROM BUFFALO WHOLE MILK

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

PAGIRE SOMNATH GANGADHAR
B.Tech (DT)

DAIRY ENGINEERING DIVISION
NATIONAL DAIRY RESEARCH INSTITUTE
(I.C.A.R.)
KARNAL-132001 (HARYANA), INDIA
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Approved by

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27.7.12

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CERTIFICATE

This is to certify that the thesis entitled **“MOISTURE SORPTION CHARACTERISTICS OF PEDA FROM BUFFALO WHOLE MILK”** submitted by **Mr. Somnath Gangadhar Pagire** 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 him under my supervision and guidance and no part of the thesis has been submitted for any other degree or diploma.

Dated: 23rd June, 2012

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

Dedicated

to

Anna

&

Aaie

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ABSTRACT

The state of water in the product plays a crucial role in the preservation of biological materials in both raw and processed states. Water activity is considered as one of the most important parameter in food preservation and processing. *Peda* is a khoa based indigenous milk product, popular in all over India. 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 *peda* prepared from buffalo whole milk at different temperature and to find out the temperature dependence of parameter of best fitted equation. Moisture sorption characteristics of *peda* 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 increased 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 *peda* was 0.85 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 13kJ/mol at 5% moisture level and then decreased. The difference between equilibrium moisture content of *peda* in adsorption and desorption was found to be significant. The hysteresis energy reduced from 67.72 kJ/kg of water at 15ºC to 32.25 kJ/kg of water at 35ºC. The monolayer moisture content of *peda* also decreased from 6.51 g/100g solids at 15ºC to 5.90 g/100g solids at 35ºC.

सारांश

उत्पाद में पानी की स्थिति जैविक सामग्री के दोनों कच्चे और प्रसंस्कृत हालात के संरक्षण में एक महत्वपूर्ण भूमिका निभाता है | पानी गतिविधि खाद्य संरक्षण और प्रसंस्करण में सबसे महत्वपूर्ण पैरामीटर के रूप में माना जाता है| पेढा एक खोया आधारित स्वदेशी दूध उत्पाद भारत में सबसे अधिक लोकप्रिय है | पानी गतिविधि को समझना और नियंत्रण सुरक्षित फूड भंडारण की स्थिति के लिए योगदान देता है और आधुनिक फूड तैयार करने का आधार है मध्यवर्ती नमी खाद्य पदार्थों के लिए विशेष रूप से महत्वपूर्ण है| इस अध्ययन के समग्र उद्देश्य भैंस पूरे दूध से तैयार किये गए पेढा की नमी अवशोषित करने के मापदंडों को अलग तापमान पर प्राप्त करना और सबसे अच्छा फिट समीकरण के पैरामीटर का तापमान निर्भरता प्राप्त करना था| गुरुत्वीय स्थैतिक विधि का उपयोग करके पेढा के नमी अवशोषित करने के विशेषताओं को १५, २५ और ३५ डिग्री तापमान पर प्राप्त किये गये| नमी सॉर्बशन 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 सॉर्बशन 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| पेढा की प्रारंभिक पानी गतिविधि २५ डिग्री तापमान पर ०.८५ पाई गयी| सॉर्बशन डेटा की नेट ऐसोस्टेरिकगर्मी क्लासुसिउस-क्लाप्रोन समीकरण का उपयोग कर से निर्धारित क़िए गए| सॉर्बशन की गर्मी शुरू में बढ़कर ५ प्रतिशत नमी के स्तर पर १३ की जुल प्रति मोल की एक शिखर मूल्य प्राप्त करने के बाद नमी के वृधि के साथ कम होती गयी| हिस्टैरिसीस ऊर्जा ६७.७२ किलो जुल प्रति किलो पानी १५ डिग्री तापमान पर पाई गयी और ३५ डिग्री तापमान पर ३२.२५ किलो जुल प्रति किलो पानी तक कम हो गयी| पेढा की एकल परत नमी की मात्रा ६.५१ ग्राम प्रति १०० ग्राम सोलिड्स १५ डिग्री तापमान पर पाई गयी और ३५ डिग्री तापमान पर ५.९० ग्राम प्रति १०० ग्राम सोलिड्स तक कम हो गयी थी|

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LIST OF ABBREVIATIONS AND SYMBOLS

a_w : Water Activity

AOAC : Association of official Analytical Chemists

ATR-MIR : Attenuated Reflectance Mid Infra Red

COST : Co-operation in the field of Scientific and Technical Research

ºC : Degree Celsius

EMC : Equilibrium Moisture Content

g : Gram

GAB : Guggnheim-Andrson-De-Boer

kg : Kilogram

mg : Milligram

ml : Milliliter

% : Percentage

R : Gas constant (8.314 J/ degree /mol)

RMS : Root Mean Square

T : Absolute temperature (degree Kelvin)

CHAPTER - 1

Introduction

Chapter 1

INTRODUCTION

Water is the main component of all the food products and stability of products depends upon the interaction of water with other components present in the product. The status of water in product plays a crucial role in the preservation of biological materials in both the raw and processed status. The simplest way of expressing such a status is the concept of water activity. It is generally accepted that the water activity is more closely related to the microbial, chemical and physical properties of food and other natural products than its total moisture content. This concept is used in correlation with food safety and quality. Water activity is considered as one of the most important parameter in food preservation and processing, thus several food preservation techniques rely on lowering the water activity so as to reduce the rates of microbial growth and chemical reactions.

Water activity has become one of the most important intrinsic property used for predicting the survival and growth of microorganisms in food (Scott, 1957), due to its direct influence on product stability and quality. Thus, the minimal water activity level for growth emerged as one of the most investigated parameters for determining the water relations of microorganisms in food. The understanding and control of water activity contributes to safer food storage conditions and general and forms the basis of much modern food formulation, especially for intermediate moisture food.

The relationship between water activity and equilibrium moisture content of food is known as moisture sorption isotherm. The moisture sorption isotherm is an extremely valuable tool for food scientists and technologist to predict potential changes in food stability. It can be used for the determination of storage conditions, packaging selection and ingredient selection.

The knowledge of sorption models of a given product is also useful in the 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 product seemed to be stable against microbial deterioration (Rehman and Labuza, 1999).

The enthalpy of adsorption and desorption can be determined with good approximation 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 provides an indication of the binding strength of water molecules to the solids and has a bearing on the energy balance of drying and freezing equation. Also the end point of drying process is generally determined by the desired water activity of the finished product.

In mixing operations and formulation work the isotherm of each component must be known in order to predict undesirable transfer of water from one ingredient to another, which would be result in rapid deterioration of final product. Packaging is the most important field of practical use of sorption isotherms. Again the slope of isotherm, the 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. An understanding of temperature dependence of sorption phenomena in food provides valuable information to characterize storage and packaging problems. The value of monolayer moisture content of food gives an indication of total number of polar groups binding water and the level of hydration, at which the mobility of small molecules becomes apparent. The importance of knowing the water activity at which the monolayer exists is that it appears to be the most stable water content for food in relation to its shelf life.

Information on moisture sorption isotherms of various traditional dairy products including khoa, burfi with sugar substitute, gulabjamun mix powder, ready to serve basundi mix and channa podo are available. Keeping in view the importance and utility of moisture sorption characteristics, the present study has been planned to determine these characteristics of indigenous milk sweet *peda* prepared from buffalo whole milk. The objectives of the investigation were:

1) Establishing moisture sorption isotherm of buffalo whole milk *peda* at 15, 25 & 35ºC.
2) Mathematical analysis of isotherm and evaluating hysteresis and thermodynamics of moisture sorption of *peda*.

CHAPTER - 2

Review of Literature

Chapter 2

REVIEW OF LITERATURE

The available literature pertaining to water activity, moisture sorption isotherm and its various models has been described in following sub headings:

2.1 PEDA
  2.1.1 Technology of Peda Processing
  2.1.2 Process Mechanization
  2.1.3 Texture and Sensory Properties of Peda
  2.1.4 Shelf life of peda
2.2 CONCEPT OF WATER ACTIVITY
  2.2.1 Water Activity And Food Deterioration
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2.3 TEMPERATURE DEPENDENCE OF ISOTHERM
2.4 THERMODYNAMIC ASPECT OF WATER ACTIVITY
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2.1 PEDA

Peda is a khoa based indigenous milk product, popular all over India. The total output of indigenous milk products is estimated to be $12 billion. This is more than half of the total market ($22 billion) of milk and milk products in India (Gupta, 2007). According to industry estimates, the production of peda exceeds that of any other indigenous milk based sweet (Aneja *et. al.,* 2002). Peda is prepared by mixing khoa with copious quantities of sugar usually in the ratio 3:1. During production peda the stir-frying process dries out the moisture. Sugar provides the preservative, giving peda a long shelf life. If desired nuts and flavouring substances could also be added. Cardamom being commonly added for the flavouring of peda. Incorporating 1-2% coca makes the chocolate pedas where as saffron peda by mixing saffron. Peda is whitish yellow in colour and has a coarse grainy texture. Its quality is determined by the quantity of sugar added, heating parameters and storage condition.

2.1.1 Technology of Peda Processing

Aneja *et. al.,* (2002) standardize a method of manufacturing of peda from khoa of 72% total solids. According to this method (Fig. 2.1) khoa with 72% TS is heated up to 60ºC and then sugar is added at the rate of 30% of khoa. At the same time flavors and nuts are added and the mixture is mixed thoroughly in planetary mixture and the peda mass is cooled to 5ºC. After cooling the peda mass is molded in different shapes and then wrapped by parchment paper and packed in cardboard boxes. Packed pedas are stored at refrigerated condition.

2.1.2 Process Mechanization

Amit and Kohli (2001) described the mechanized production of peda by SSHE (Scraped Surface Heat Exchanger). The results showed that feeding of khoa in semi-solid form at a temperature of 40ºC formed a thin film of product inside SSHE and helped in the forward movement of product leaving behind very less quantity of product inside SSHE. Higher rotor speed increased free fat content and increase in steam pressure decreased penetration value thus causing peda harder. The optimum parameter for best quality peda were found to be 125 rpm, 2kg/cm^2, 25 kg/hr feed rate and addition of sugar @ 30% on khoa basis.

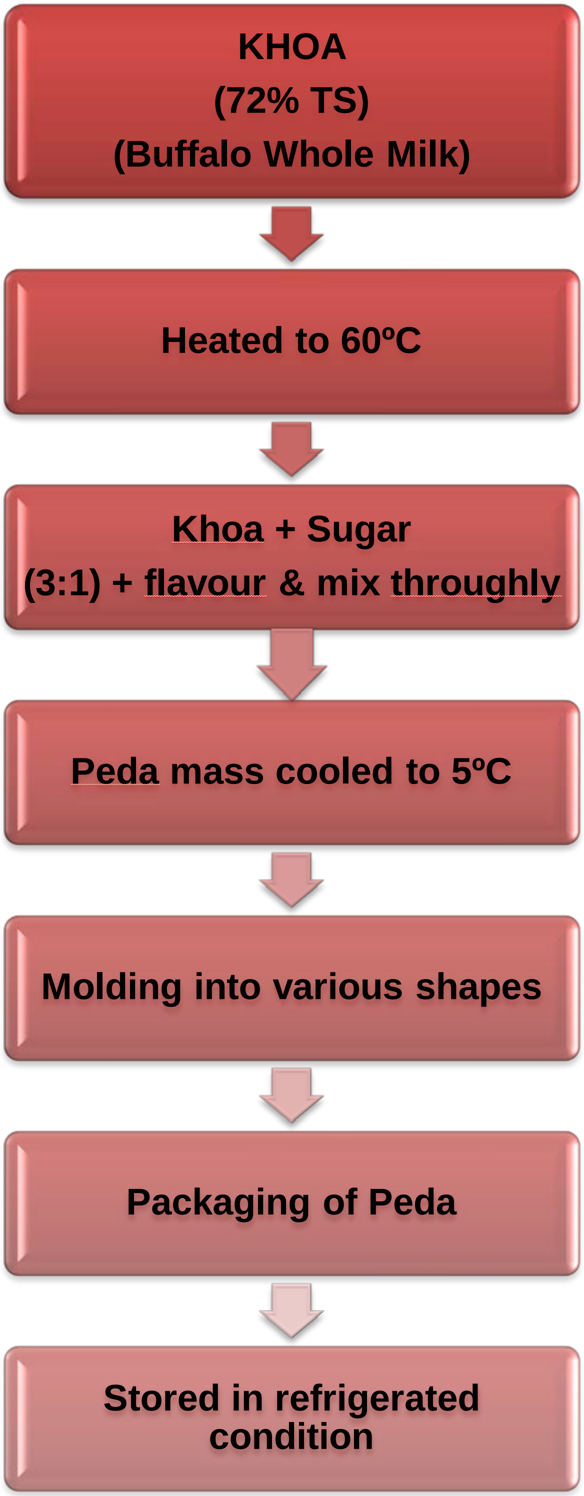

Fig. 2.1 Manufacturing Process of Peda

2.1.3 Texture and Sensory Properties of Peda

Patel *et al.* (2006) studied the textural properties of two types of peda collected from market viz. prepared by traditional method and mechanical method using an Instron Universal Testing Machine model-1000. They observed that the product manufactured by traditional method was almost 2 to 3 times harder than mechanical method; however the difference was not significant. All other rheological parameters were marginally different in both the manufacturing process of peda.

Dewani and Jayprakasha (2002) studied the effect of addition of whey protein concentrate on sensory characteristics of peda. The result shown that increasing level of WPC up to 40% showed increasing colour and appearance, body and texture and overall acceptability score of peda whereas flavor score increased up to 50% WPC level. These workers (2004) also optimized the process for production of peda from pre concentrated milk by reverse osmosis and vacuum evaporation. Colour, appearance, body and texture scores of peda prepared from RO pre-concentrated milk improved up to 40% TS levels with heat treatment of 90°C for 10 min.

2.1.4 Shelf Life of Peda

Peda is expected to have good shelf life due to low moisture content and high sugar content. The sugar to water ratio of finished product should be at least 1.5:1 giving an osmotic pressure of 140 atmospheres which is susceptible to microbial spoilage due to unhygienic conditions adopted during manufacturing and handling and its surface contamination (De and Ray, 1952).

Biradar *et al.* (1985) studied on shelf life extension of peda by packaging. They found that packaging in 100 and 300 gauge low density polyethylene pouches reduces weight loss, browning and free fatty acid development and deterioration of flavor, odor and acceptability of peda during storage. Peroxide value was not influenced by LDPE packaging. LDPE-300 was more effective in controlling weight loss, browning and FFA formation than LDPE-100. Film thickness however did not influence on the organoleptic attributes significantly.

2.2 CONCEPT OF WATER ACTIVITY

The importance of water to all life is well recognized as well as the role in controlling the growth of microorganism in food and other biological systems. The simple way for 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. This active water is responsible for the growth of spoilage bacteria, chemical reactions and enzymatic activities. In case of moisture sensitive dairy products, especially dehydrated products water is most important characteristics that affect the physical, chemical, microbial and sensory properties.

Thus it is the state of water rather than the total water content, which is important as far as microbial proliferation is concerned. It has been observed that the state of water is related to the vapour pressure of food. Greater the proportion of free water present greater the vapour pressure and vice versa. Increased bound water reduces vapour pressure (Scott, 1975).

The 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 the food. Hence water activity can be defined as the ratio of vapour pressure of water in food and the vapour pressure of pure water at the same temperature and pressure conditions (Labuza, 1968).

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

$$Aw = \frac{P}{P_o} = \frac{ERH}{100}$$

Where,

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

2.2.1 Water Activity and Food Deterioration

Maximum stability of natural products has been associated with minimum total moisture until about 30 years when definite studies in shelled walled nuts demonstrated that there was a narrow optimum moisture range corresponding to a broader water activity range above and below which kernels deteriorated at more rapid rate (Rockland, 1987).

It is now generally accepted that water activity is more closely related to the physical, chemical and biological properties of foods and other natural products rather than to total moisture content. Specific changes in color, aroma, flavor, texture, stability and acceptability of raw and processed food products have been associated with relatively narrow water activity range. Water activity may have direct uncomplicated effect upon various chemical reaction (Labuza, 1980), enzymatic reaction (Schwimmer, 1980) and proliferation of micro-organisms (Troller and Christians, 1978).

A number of other examples of phenomenon have also been reported. Kapsalis (1973) reported a sharp maximum force for shearing freeze-dried beef corresponding to 0.8-0.85 water activity. Koury and Spinelli (1975) observed optima for the emulsifying capacity of protein and dried protein carbohydrate mixture. In a classical study with a loss of free amino nitrogen occurred during storage at 37°C in a casein glucose mixture at intermediate water activity range. Water activity optima for non-enzymatic browning reactions were corroborated in systematic studies by Karle and Labuza (1968) using model system. Work in this important area has been extended and reviewed by Resrick and Chirife (1979), Eicher and Ciner Durek (1980) and Labuza and Sltmarch (1980).

2.2.2 Moisture Sorption Isotherm

Generally food when kept in different relative humidity absorb or desorbemoisture depending on their water activity (Kapsalis, 1987). When water activity is less than surrounding humidities the product will adsorb moisture and when reverse is the case it will desorb the moisture. Therefore when a product is equilibrated with different relative humidity the water content in the product on solid basis plotted on ordinate against the value of humidity on abscissa gives the 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.* (1940) 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 swellable 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).

Moisture Sorption isotherm is explained by three regions. Region I describers the strongly bound water with an enthalpy of vaporization considerably larger than that of pure water. In many aspects it behaves essentially as a part of solids. It is generally understood that these first water molecule are sorbed at the active polar groups in solids (Pauling, 1945). Region II represents water fraction less firmly bound than the first. Region 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.

Moisture sorption isotherm illustrates the steady-state amount of water held by the food solids as a function of a_w at constant temperature (Labuza, 1968). Thus, the 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).

The advantage 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.

2.2.3 Moisture Sorption Isotherms of Foods

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%.

Berline *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.

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 (Labuza, 1968). 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.

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 warer/ 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 them decrease.

Sawhney *et al.,*(2010) studied the moisture sorption characteristics of dried acid casein from buffalo skim milk at 25, 35 and 45^{o}C 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.

2.2.4 Isotherm Models

There are various models with corresponding mathematical equations for predicting or data fitting of sorption isotherm of foods. The mathematical expression based on two- and three- parameter models are the most commonly used. Due to the complex nature of foods, no single model is general enough to represent the sorption isotherm of foods. BET and GAB models are most commonly used in predictions of sorption isotherms of foods. Iglesias and Chirife (1976) reviewed several equations for modeling equilibrium moisture content and reported that some models were adequate to characterize the sorption behavior of particular foods for the given range of temperature and Aw or relative humidity.

The water sorption isotherm at 30ºC of pre cooked beef previously dried at three different temperatures was determined. 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.

The 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 the 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. The 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 45°C. It was found that GAB equation has better fit compared to other models.

Prateek. (2005) studied the desorption isotherm of ready to use Basundi mix in the temperature range of 5-45°C 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 45°C 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. The 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 ISOTHERM

The water activity shift by temperature at constant moisture content is due to the 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. Moreover, for constant moisture contents, the amount of bound water is also more easily desorbed with rising temperatures, wherein mobility of the water molecules as well as dynamic equilibrium between vapor and adsorbed phase are affected.

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 due to 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.

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 THERMODYNAMIC ASPECT OF WATER ACTIVITY

The thermodynamic properties of foods relate the concentration of water in the food to its partial pressure, which is crucial in analysis of heat and mass transport phenomenon during dehydration. They determine the endpoint to which the food must be dehydrated in order to achive a stable product with optimal moisture content, and the minimum amount of energy required to remove a given amount of water from food (Aviara and Ajibola, 2002). The thermodynamic functions are readily calculated from sorption isotherms which enables interpretation of experimental results in accordance with the theory (Iglesias *et al.,* 1976). The functions include differential heat of sorption, differential entropy, integral enthalpy, integral entropy and spreading pressure.

Isosteric heat of sorption is used as an indicator of the state of water adsorbed by the solid particles (Fasina *et al.,* 1997). The state of water adsorbed is a measure of the physical, chemical and microbial stability of biological materials under storage (Labuza, 1968). Knowledge of the 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).

2.5 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).

The hysteresis in the sorption isotherm results from the presence of network of pores and voids in foods. The physical phenomenon, such as glass transition and swelling of food matrix, also lead to sorption hysteresis. In this respect, the ink bottle theory and glass-transition theory (Bell and Labuza, 2000) explain that the hysteresis in sorption isotherm is inevitable.

The transition between a glassy and rubbery state of a material can also led to hysteresis. Moisture adsorption into a glassy material is usually very slow due to much reduced moisture diffusivities and restricted moisture mobility. The food sample may be fail to reach its equilibrium moisture content within the experimental time frame. This leads to a lower moisture content for a given a_w than if equilibrium was reached. However, food samples are usually in rubbery state during the desorption process and have an inherently higher moisture mobility due to higher diffusion coefficient. This allows rubbery samples to reach equilibrium faster, which usually leads to higher moisture content (desorption) than for the glassy state during adsorption (Bell and Labuza, 2000).

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 the temperature, a 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).

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 Methods

Chapter 3

MATERIALS AND METHODS

The experimentation and the analysis of the present study carried out for the prediction of water activity of Peda and investigation was carried under following headings:

3.1 TEST SAMPLE

3.2 DETERMINATION OF CHEMICAL COMPOSITION OF PEDA

- 3.2.1 Determination of Moisture
- 3.2.2 Determination of Fat
- 3.2.3 Determination of Protein
- 3.2.4 Determination of Lactose and Sucrose
- 3.2.5 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 of Sorption
- 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

3.1 TEST SAMPLE

Peda from buffalo whole milk was chosen as test sample for present study. Test sample was prepared by using a standardized method given by Aneja and Mathur in 2002 as shown in Fig. 2.1. Peda was prepared in steam jacketed kettle . Peda from buffalo whole milk (Fig. 3.1) was used to determine moisture sorption characteristics.

Fig. 3.1 Peda from buffalo whole milk

3.2 DETERMINATION OF CHEMICAL COMPOSITION OF PEDA

3.2.1 Moisture

Mojonnier method as described in IS:2785 (1964) for determination of moisture in cheese was used for peda with slight modifications.

About 20 gm of previously washed and dried sand was weighed into aluminum dish, allowed to dry further in an oven at 100ºC and weighed to the nearest of 1 mg constant weight. 5 gm of peda sample was transferred in dish and 5 ml of distilled water was added to it. The contents were mixed thoroughly in form of a paste with the help of glass rod. The dishes were then transferred to thermostatically controlled water bath at 100º ± 1ºC for 30 min. and later transferred to a hot air oven maintained at 100º ± 1ºC. The drying was controlled till the solid mass of the dishes turned to be light brown and difference between the two successive weighing was not more than 1 mg. The result was expressed on the basis of 100 gm of peda as follows.

$$\text{Moisture(wb)}\ \% = \frac{W_1 - W_2}{W_0} \times 100 \qquad \text{……….} (3.1)$$

Where,

W_1 = weight of sample along with dish etc before drying (gm)

W_2 = weight of sample along with dish etc after drying (gm)

W_0 = weight of sample taken (gm)

3.2.2 Fat

Fat in peda was determined by Rose – Gottlieb method for milk as described in SP: 18 (Part XI), 1981with some modifications.

Five gm of peda sample was accurately weighed into small beaker and made to paste with an equal amount of warm (65ºC) distilled water. Two ml of concentrated ammonia solution (sp. gr. 0.88) and 9 ml of distilled water were added. The contents were swirled gently, colled and 10 ml ethyl alcohol (95% v/v) was added.

The contents were then completely transferred to the Mojonnier fat extraction tube and shake for 2 min. twenty five ml each of diethyl ether (Sp. Gr. 0.721; peroxide free) and petroleum ether (40º - 60ºC BP) were added and the tube was closed with a wet cork and shake vigorously for 1 min. The tube was centrifuged for 1 min to separate the ethereal layer from the aqueous layer and the supernatant liquid was decanted in clean, dry previously weighed aluminium dish. Extractions were repeated twice using 15 ml of diethyl and petroleum each time. The solvents were distilled off and dish heated in the oven at 98º - 100ºC, cooled and weighed. Heating and weighing were repeated till weighing did not show a loss in weight by more than 1 mg. Percent of fat by weight in the sample was calculated as follows;

$$\text{Fat}\,\% = \frac{\text{Weight of fat extracted}}{\text{Weight of sample}} \times 100 \qquad \ldots\ldots\ldots \quad (3.2)$$

3.2.3 Total Protein

The total protein content of peda was determined by micro Kjeldahl method.

Accurately weighed 200 mg of peda sample was transferred to a kleltec digestion tube and digested after adding one digestion tablet (1.5 g K_2SO_4 and 0.0075 g Se) and 5 ml concentrated H_2SO_4 till the contents became clear. The contents of the flask were cooled and then distilled in the distillation apparatus. About 25 ml of saturated boric acid solution containing 4 drops mixed indicator was taken in 100 ml conical flask.

Approximately 65 to 70 ml of distillate were collected in a 100 ml conical flask. The contents of the flask were titrated against 0.02N HCl. A blank determination using distilled water in place of sample was also carried out. The total nitrogen and percent protein were calculated as follows;

$$\text{Total Nitrogen \%} = \frac{(X-Y)N\times 14.007\times 100}{W} \qquad \dots\dots\dots\dots \text{(3.3)}$$

Where,

X = ml of HCl required for sample

Y = ml of HCl required for blank

N = Normality of HCl used

W = Weight of sample in mg

Percent Total Protein = Percent Total nitrogen × 6.38

3.2.4 Lactose and Sucrose

Lactose and sucrose were estimated as per the procedure described in (BIS SP PART XI - 1981) for *burfi* with slight modifications.

Weighted accurately 40 gm sample of peda and transferred in 100 ml beaker. Added 50 ml of hot water at 80-90ºC to it and mixed and transferred the contents to a 250 ml volumetric flask and rinsed the beaker with hot water to make the volume to about 120-150ml. the contents in the volumetric flask were mixed and cooled to room temperature followed by addition of 5 ml of 10% dilute ammonia and it was allowed to stand for 15 min. the exact equivalent of 5 ml of 10% acetic acid was added to neutralize the 12.5 ml of potassium ferrocyanide solution and mixed again. The contents were made up to 250 ml mark using distilled water and allowed to settle and it was filtered through Whatman filter paper No. 1. The filtrate was marked as B1. From B1 50 ml was taken into 100 ml volumetric flask and 5 ml of concentrated HCl was added followed by heating at 68ºC for 5 minutes. It was cooled and neutralizes with 50% NaOH and made up to 100 ml with distilled water and was marked as A1. The solution marked as A1 was diluted 20 times while B1 was diluted 4 times and were marked as A2 and B2 respectively. Both the solutions were taken into a burette and titrated against the mixture of 5 ml Fehling1 and Fehling 2 solutions were added with a mixed indicator. Similarly standard lactose and sucrose were taken and titrated.

The lactose and sucrose contents in peda samples were calculated as follows;

$$\text{Lactose} = \frac{\text{Titre value for standard lactose} \times 5 \times 2}{\text{Titre value for B2}} \qquad \ldots\ldots \text{ (3.4)}$$

$$\text{Sucrose(\%)} = \frac{20\ W_1}{W_2}\left[\frac{2f_2}{V_2} - \frac{f_1}{V_1}\right] \qquad \ldots\ldots \text{ (3.5)}$$

Where,

W_1 = weight in mg of sucrose corresponding to 10 ml Fehlings solution

W_2 = weight in gm of the material taken for the determination

f_1 = dilution factor for solution A_2 from A_1

V_2 = volume in ml of solution A1 corresponding to 10 ml of Fehling’s solution

f_2 = dilution factor fr solution B_2 from B_1

V_1 = volume in ml of solution B_2 corresponding to 10 ml of Fehling’s solution

3.2.5 Acidity (% lactic acid)

A.O.A.C (1975) method for cheese was adopted for peda for determining acidity in terms of percent lactic acid. Two gm of peda sample was weighed into a porcelain dish. The product was rendered into a fine paste using 3 ml of hot distilled water (65°C). 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 peda.

$$\text{Lactic Acidity (\%)} = \frac{10-\mathrm{V}}{\mathrm{W}} \times 0.9 \qquad \text{……….. (3.6)}$$

Where,

V = Volume of 0.1 N HCl required for titration

W = Weight of Peda sample

3.2.6 Total Ash

About 2 gm of peda sample was weighed accurately in silica dish and ignited on a laboratory Bunsen burner with final incineration in muffle furnace at 550ºC for 2 hr (AOAC, 1975). Constant weight of ash was considered to have reached when the difference in the two consecutive weighing after repeated ignition was less than 0.2 mg. ash content was expressed as percent of the gross sample of peda.

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 this study. The sorption device (shown in fig. 3.2) 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.

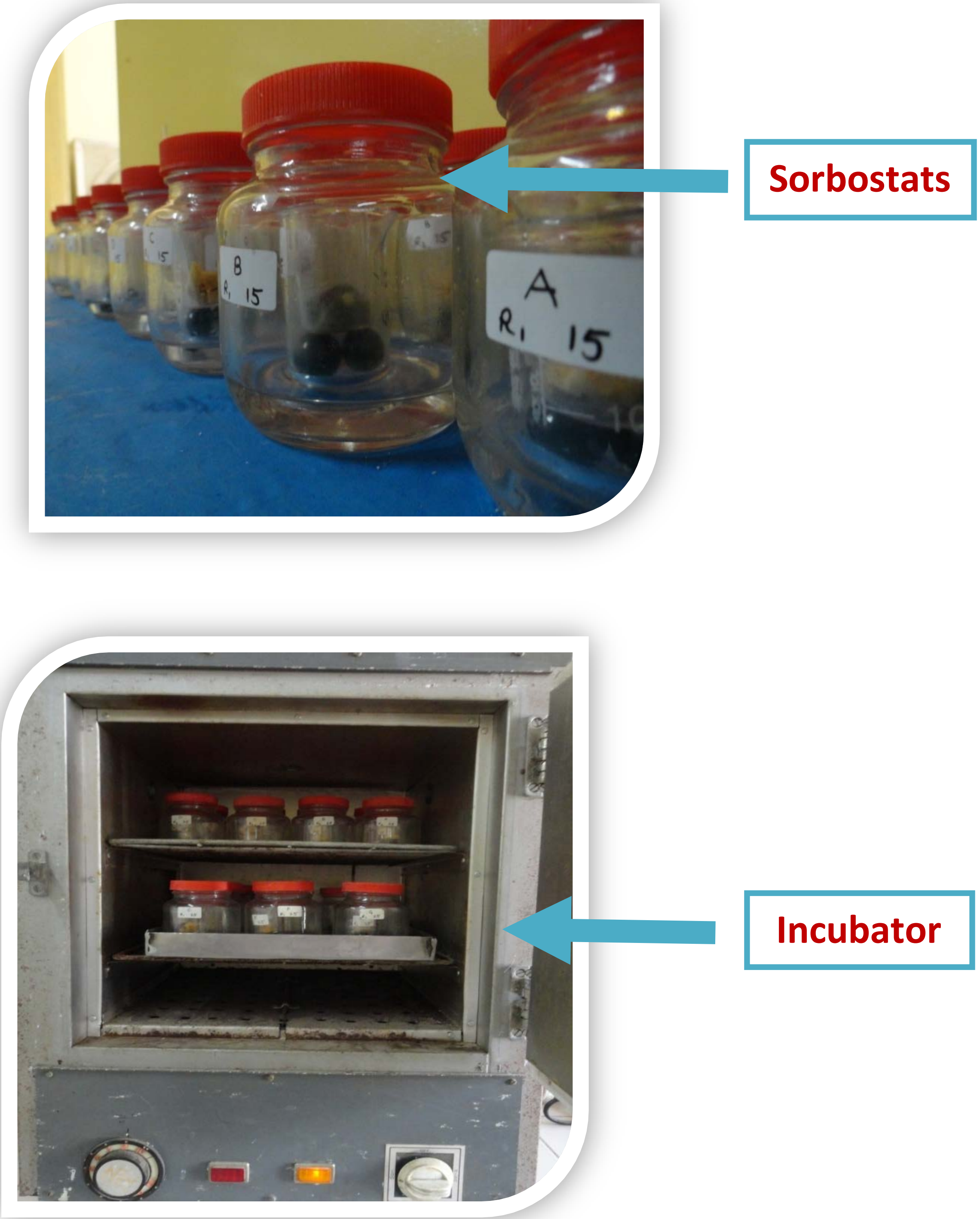

Fig. 3.2 Experimental Set-up for Sorption Study

3.3.2 Selection of Salt for Maintaining Different Humidity

Eight reagent grade salt slurries, namely (lithium chloride, magnesium chloride, magnesium nitrate, ammonium sulphate, potassium bromide, potassium chloride, barium chloride and potassium sulphate) were chosen (Greenspan, 1977). The salts were dissolved in distilled water at 100ºC 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
$LiCl.H_2O$	0.13	0.11	0.11
$MgCl_{2.}6H_2O$	0.33	0.33	0.32
$Mg(NO_3)_{2.}6H_2O$	0.53	0.52	0.51
$(NH_3)_2 SO_4$	0.79	0.79	0.79
KBr	0.85	0.83	0.81
KCl	0.87	0.86	0.84
$BaCl_2.2H_2O$	0.92	0.90	0.88
K_2SO_4	0.97	0.97	0.96

3.3.3 Maintenance of Temperature

A set of three temperatures viz; 15, 25 and 35ºC were selected for the study. Constant temperature cabinets (Fig. 3.2) were used for maintaining these temperatures. Effect of temperature on water activity of Peda 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

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 sorbostats, containing saturated salt slurries. Experiment was conducted in triplicates for best results. The sorbostats containing samples were kept at temperatures of 15, 25 and 35^{o}C.

The desorption isotherm were determined by hydrating samples in desiccators over distilled water at room temperature to approximately 40% (dry basis) moisture content. Hydrated samples were weighed in weighing beakers.

To prevent mold growth, about 0.1mg of potassium sorbate was added to each peda 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 aw 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.

$$M = \frac{(W_2 - W_1) + m}{(W_1 - m)} \times 100 \qquad \text{……..} \quad (3.7)$$

Where,

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

W_1 = Initial weight of sample (gm)

W_2 = Final weight of sample (gm)

m = Initial Moisture content of sample (gm)

3.4 FITTING OF ISOTHERM EQUATIONS

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

$$a_w = e^{\left[-a/W^b\right]} \qquad \ldots\ldots \quad (3.8)$$

OSWIN

$$W = a\left\{\frac{a_w}{1-a_w}\right\}^b \qquad \ldots\ldots \quad (3.9)$$

CAURIE

$$\ln\frac{1}{W} = \ln\frac{1}{CW_m} + \frac{2C}{W_m}\ln\frac{1-a_w}{a_w} \qquad \ldots\ldots \quad (3.10)$$

MODIFIED MIZRAHI

$$W = \frac{a + a_W\,(ca_W + b)}{a_W - 1} \qquad \ldots\ldots \quad (3.11)$$

GAB

$$W = W_m\,\frac{Cka_w}{(1-ka_w)\left[1-ka_w+Cka_w\right]} \qquad \ldots\ldots \quad (3.12)$$

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

$$\frac{a_W}{W} = aa_w^2 + ba_w + c \qquad \text{…… (3.13)}$$

Where,

$$a = \frac{k}{W_m}\left[\frac{1}{C-1}\right] \qquad \text{….. (3.14)}$$

$$c = \frac{1}{W_m Ck} \qquad \text{........... (3.15)}$$

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

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. 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_0, 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 %).

$$RMS\% = \sqrt{\frac{1}{n}\left[\sum_{1}^{n}\left(\frac{w_{EXP} - w_{CAL}}{w_{EXP}}\right)^{2}\right]} \times 100 \qquad \text{……. (3.17)}$$

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.

$$\ln\left(\frac{a_{wT1}}{a_{wT2}}\right)_{w} = \frac{\Delta Hw}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{………. (3.18)}$$

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 -ΔH/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:

$$W_m(T) = W'_m \,.e^{\Delta H'/RT} \qquad \text{….} \qquad (3.19)$$

$$G(T) = G'\,.e^{(H_1 - H_m)/RT} \qquad \text{…..} \qquad (3.20)$$

$$K(T) = K'\,.\,e^{(H_L - H_m)/RT} \qquad \text{……} \qquad (3.21)$$

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 peda 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

$$A = (D-A) / D \qquad \text{………} \qquad (3.22)$$

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):

$$\Delta G = RT \int_{O}^{U} ln\, pdw \qquad \text{………} \qquad (3.23)$$

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.

CHAPTER - 4

Results and Discussion

Chapter – 4

RESULT AND DISCUSSION

The results of the present study and their discussions are presented in following sub-headings.

4.1 CHEMICAL ANALYSIS

4.2 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 PARAMETER

4.6 NET ISOSTERIC HEAT OF SORPTION

4.1 CHEMICAL ANALYSIS OF PEDA

The composition of *peda* prepared from buffalo whole milk which was used as test sample for present study, determined by standard methods is presented in Table 4.1.

Table 4.1. Composition of *peda* prepared from buffalo whole milk

Parameter	**Peda from Buffalo Whole Milk**
Moisture %	15.12 %
Fat %	29.00 %
Protein %	16.10 %
Lactose %	15.06 %
Sucrose %	21.34 %
Ash %	2.67 %
Titratable Acidity % (LA)	0.71 %

4.2 SORPTION ISOTHERM OF PEDA

4.2.1 Adsorption and Desorption Isotherm of Peda

Moisture sorption isotherm of *peda* prepared from buffalo whole milk at 15, 25 % 35°C were estimated. Adsorption and desorption isotherms of *peda* measured at above temperature are shown in fig. 4.1 to 4.6. All sorption isotherm demonstrate an increase in equilibrium moisture content with increasing water activity and beyond 0.9 a_w the increase in EMC was sharp. This behavior is manifested in the form of a sigmoid shape curve, thus reflecting a **Type II** isotherm (Brunauer *et al.* 1940), which is typical to most of the foods. In all isotherms the moisture uptake was slow up to a water activity of 0.35 aw, it was moderate between 0.35 to 0.85 aw and the equilibrium moisture content increased sharply beyond 0.85 aw. Similar behaviour was observed for desorption isotherms. The isotherms showed that the product adsorbed proportionately more water towards the later part of the curve.

Similar types of observations were found by Lin *et al.* (2005) for milk powders, Sawhney *et al.* (2010) for dried acid casein from buffalo whole milk, Govardhan (2006) for gulabjamun mix powderand Sawhney *et al.* (1991) for khoa. Prateek (2005) observed the steep rise in EMC at higher water activity in basundi.

4.2.2 Effect of temperature on isotherm

The effect of temperature on adsorption and desorption isotherm of peda are shown in fig 4.7 & 4.8. It may be seen that from 0.33 to 0.88 a_w all the three curves of adsorption and desorption were clearly distinguishable. Above 0.88 a_w and below 0.33a_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. The effect of temperature on the sorption isotherm is of great

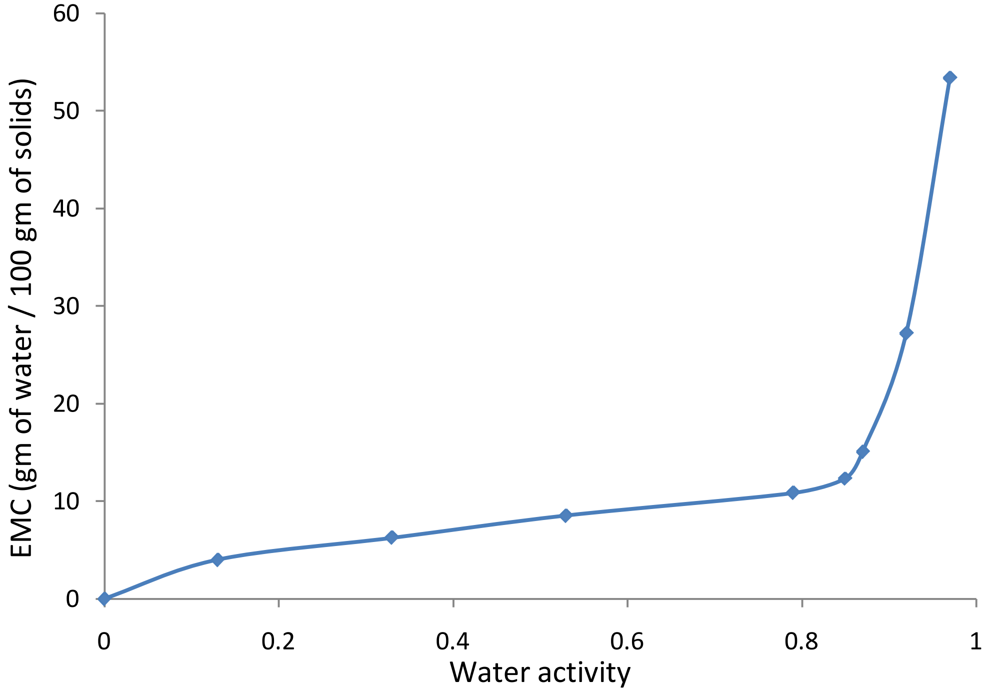

Fig. 4.1. Moisture Adsorption Isotherm of Peda at 15^{0}C

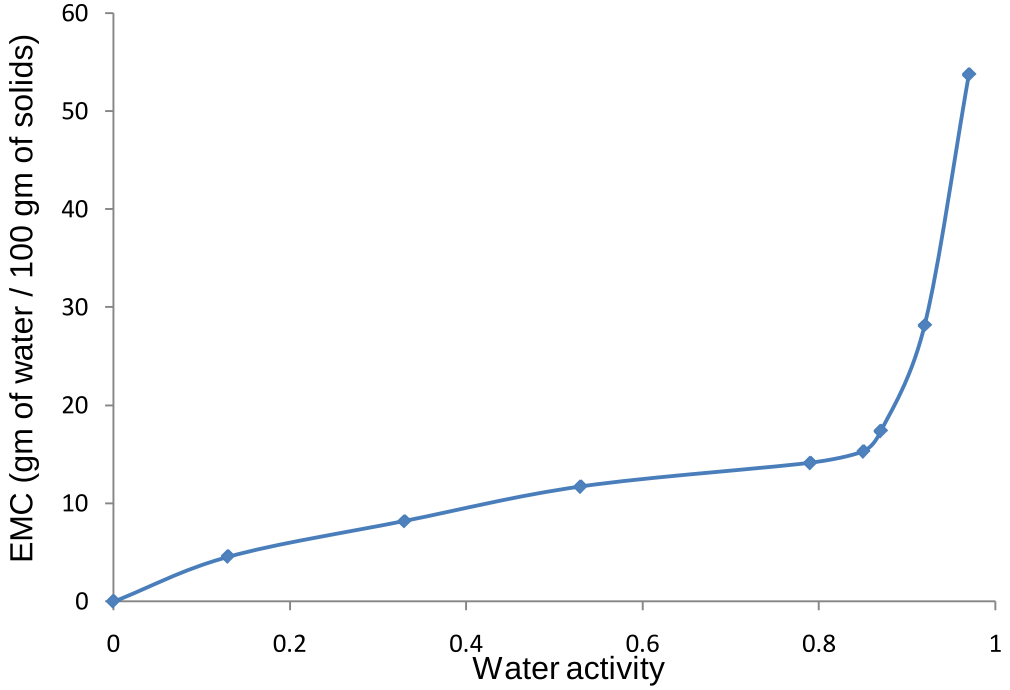

Fig. 4.2 Moisture Desorption Isotherm of Peda at 15^{0}C

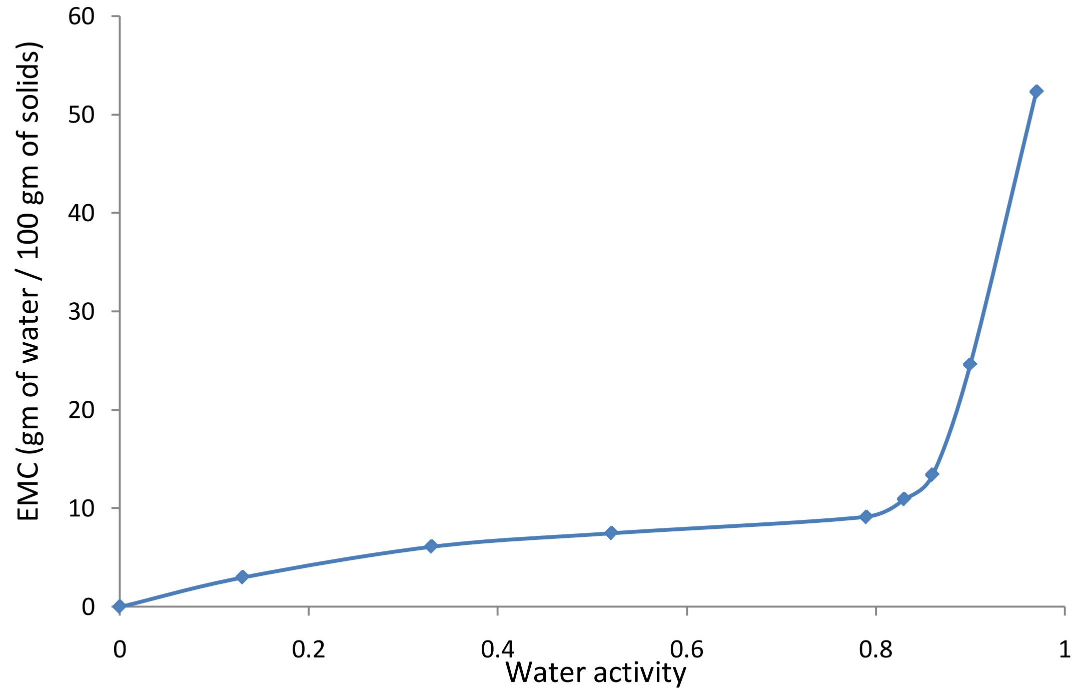

Fig. 4.3 Moisture Adsorption Isotherm of Peda at 25^{0}C

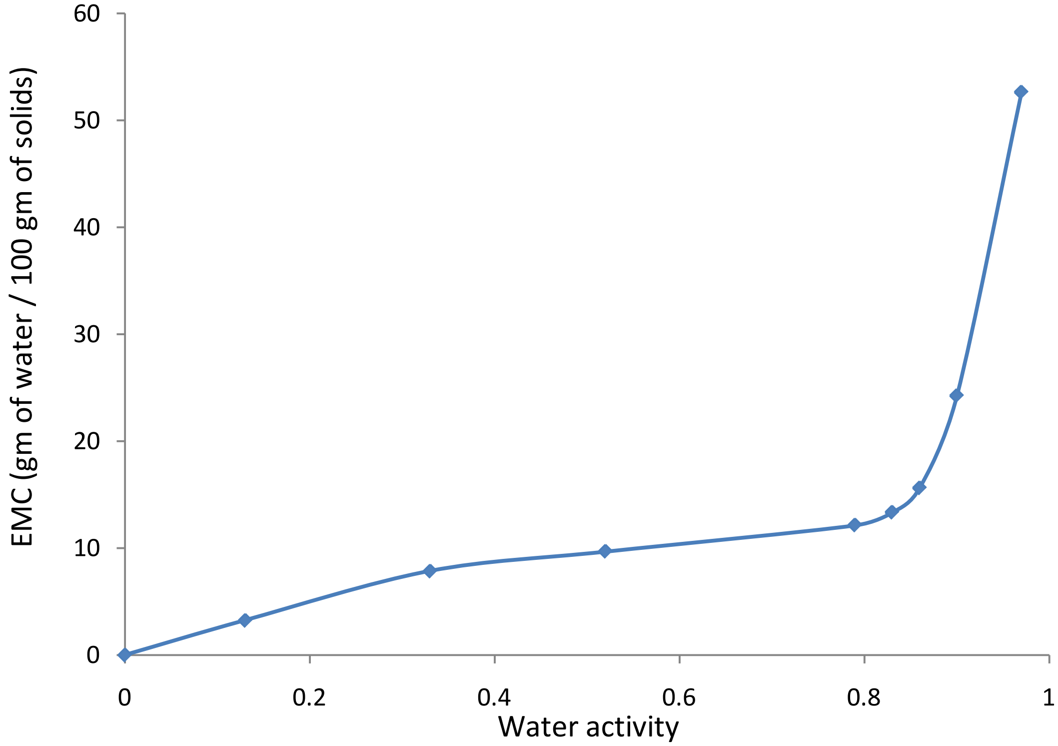

Fig. 4.4 Moisture Desorption Isotherm of Peda at 25^{0}C

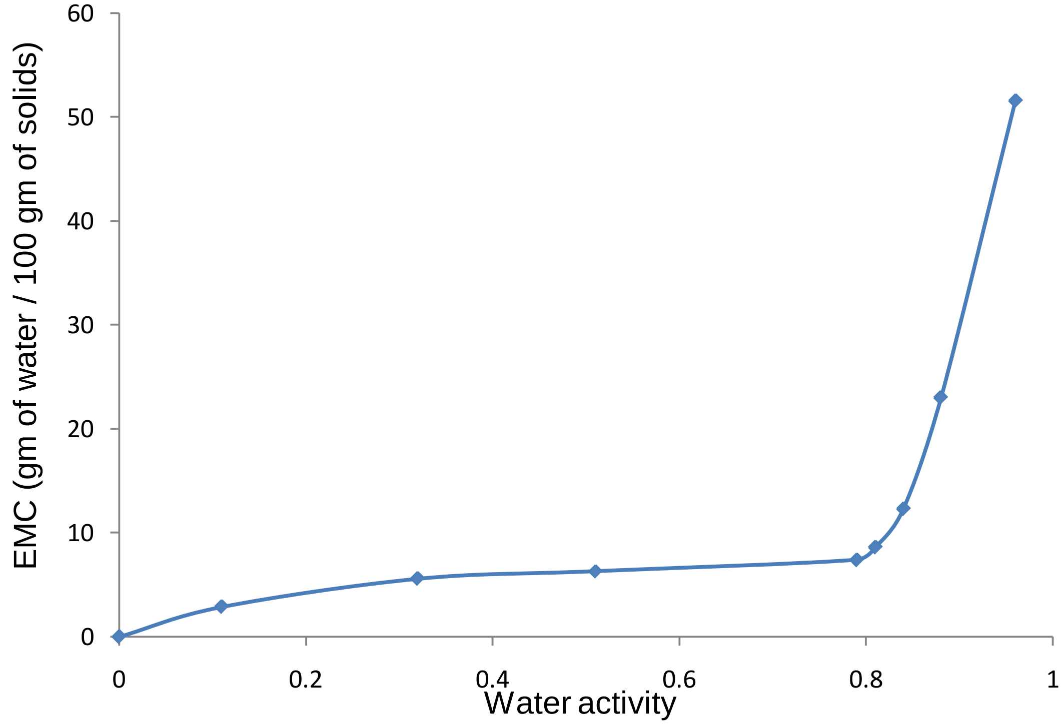

Fig. 4.5 Moisture Adsorption Isotherm of Peda at 35^{0}C

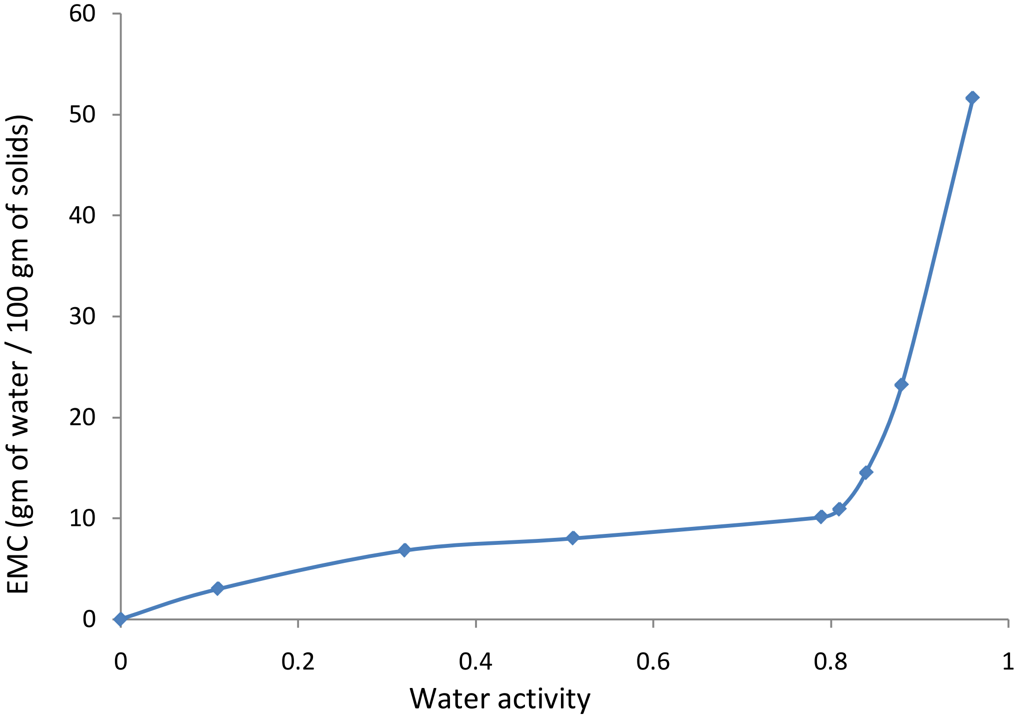

Fig. 4.6 Moisture Desorption Isotherm of Peda at 35^{0}C

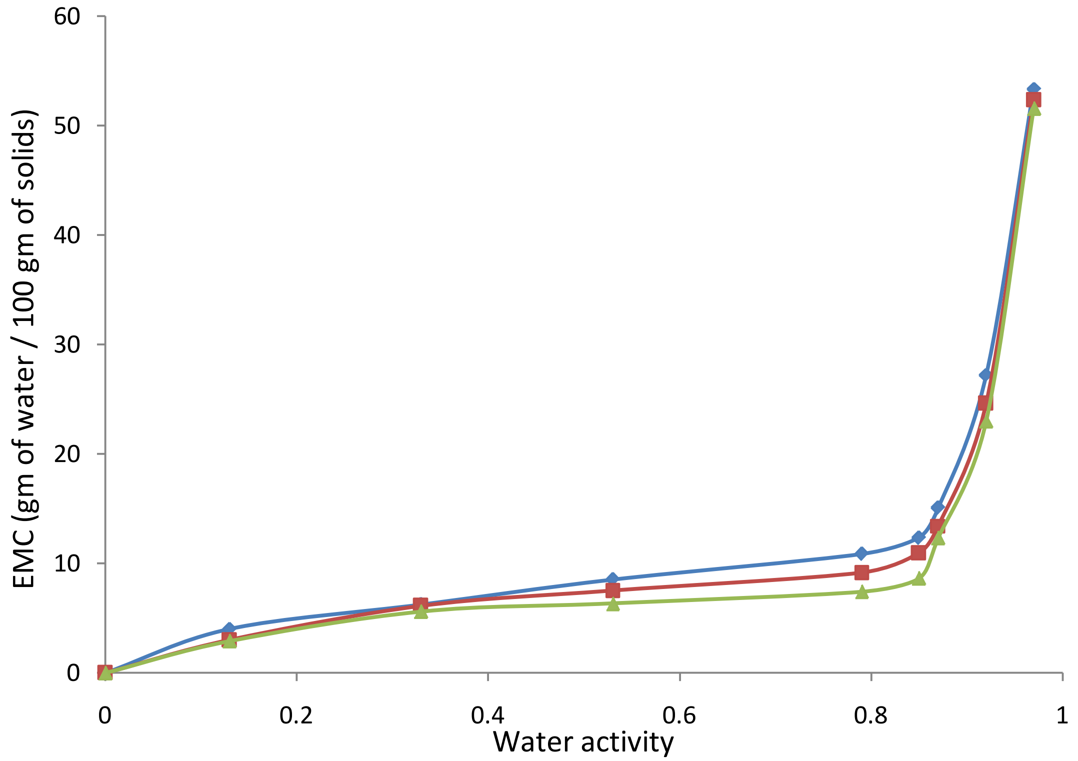

Fig. 4.7 Moisture Adsorption Isotherm of Peda at

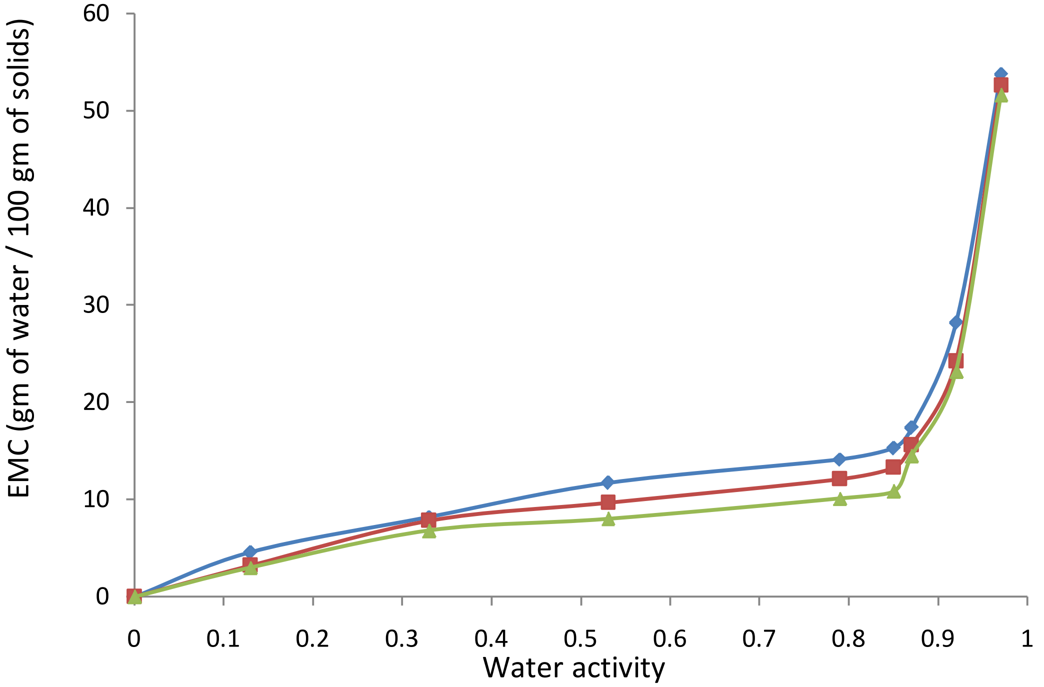

Fig. 4.8 Moisture Desorption Isotherm of Peda at

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 revealed that the effect of temperature on moisture content was statistically significant (P>0.05) over the temperature range of 15 – 35^{o}C. Foster *et al*. (2005) has observed no obvious temperature dependence in isotherm of high miceller casein powder measured between 4-37^{o}C but found the isotherm at 50^{o}C to be significantly lower at water activities above 0.2.

4.3 EVALUATION OF MOISTURE SORPTION HYSTERESIS

The moisture sorption hysteresis of *peda* prepared from buffalo whole milk at 15, 25 & 35^{o}C shown in fig 4.9 to 4.11. The hysteresis effect exhibited by *peda* shows that the adsorption and desorption isotherms were distinctly apart from each other. The hysteresis loop was 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 became minimum beyond 0.85 a_w and the adsorption and desorption isotherm of *peda* coincides with each other at about 0.91 a_w at 15^{o}C, 0.9 a_w at 25^{o}C and 0.88 a_w at 35^{o}C. Maximum hysteresis was observed between 0.30 to 0.85 a_w.

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 peda 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 SPSS to compare moisture content sorbed by the samples at different temperatures during the adsorption and desorption. Paired t-test revealed that the adsorption and desorption differ significantly at all the three temperatures with $t_{0.05} = 4.66$ at 15ºC, $t_{0.05} = 3.29$ at 25ºC, and $t_{0.05} = 3.44$ at 35ºC. 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. 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 are shown in Figure 4.12. The graphical integration of area under this curve gave the hysteresis units. The total hysteresis in peda was 1.55 units at 15ºC. 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 peda from buffalo whole milk, the effect of increasing the isotherm temperature was found decreasing the total hysteresis from 1.55 units at 15ºC to 1.35 at 25ºC and 1.21 at 35ºC. It also resulted in limiting the span of the loop along the isotherm.

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 peda was 0.303 at 15ºC. It reduced with increase in temperature to 0.284 at 25ºC and 0.253 at 35ºC. 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 peda are in agreement to this.

Table 4.2 ANOVA (Analysis of variance) for effect of temperature on equilibrium moisture content of Peda

Adsorption ANOVA (5% LS)						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F critical*
Water Activity	5470.166	7	781.4522	1777.248	1.53×10^{-19}	2.764199
Temperature	24.60313	2	12.30157	27.97731	1.29×10^{-5}	3.738892
Error	6.155772	14	0.439698			
Total	5500.924	23				
Desorption ANOVA (5% LS)						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F critical*
Water Activity	5235.13	7	747.8757	1629.328	2.81×10^{-19}	2.764199
Temperature	20.29926	2	10.14963	22.11207	4.65×10^{-5}	3.738892
Error	6.42612	14	0.459009			
Total	5261.855	23				

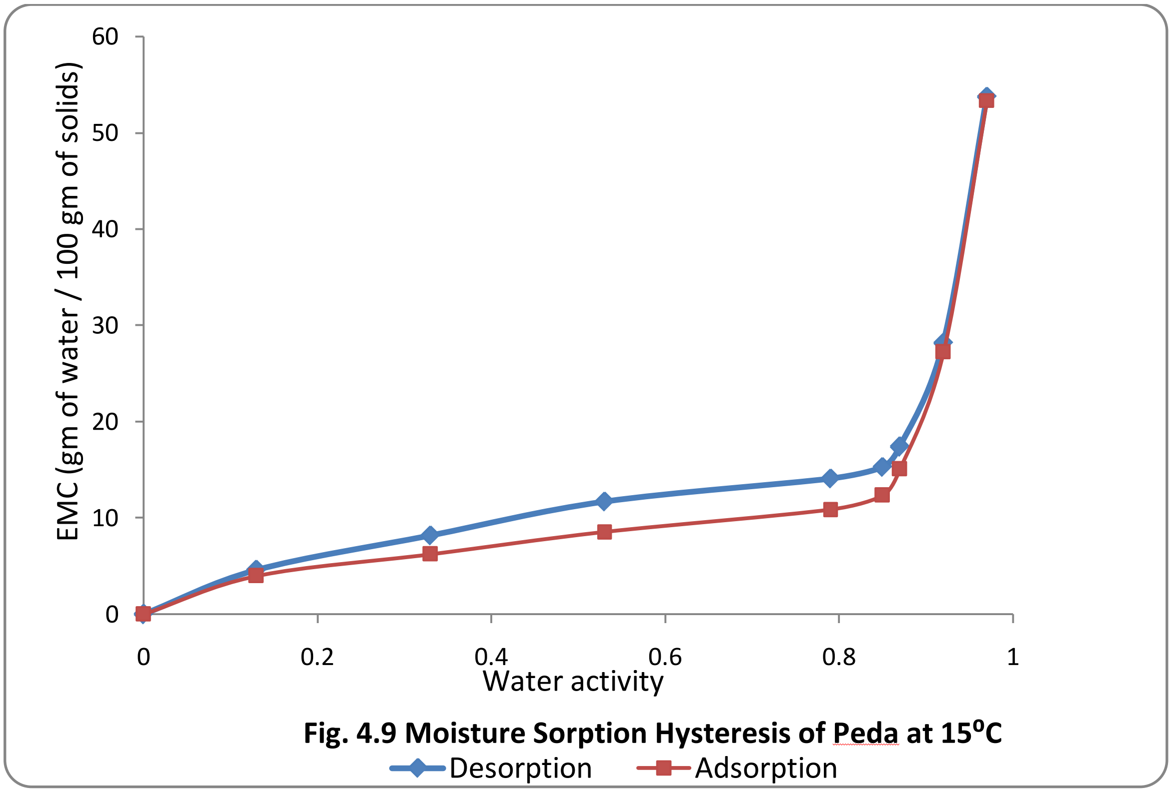

Fig. 4.9 Moisture Sorption Hysteresis of Peda at 15^{o}C

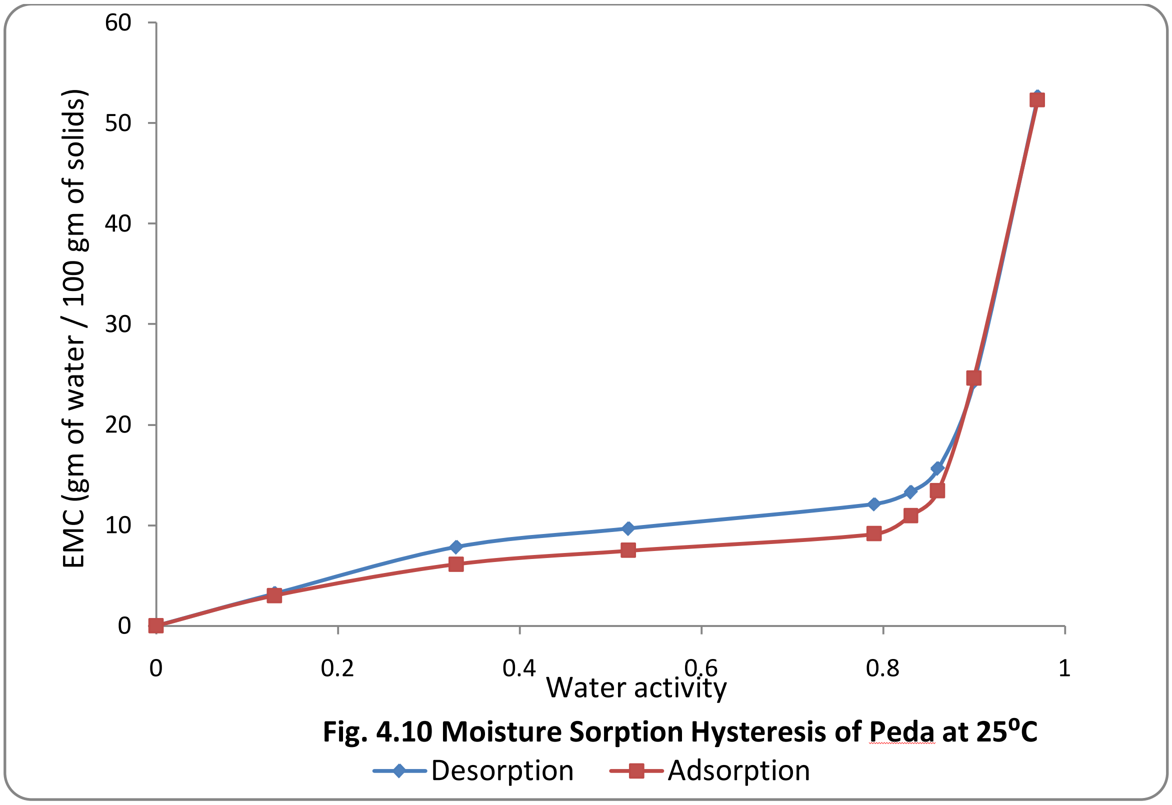

Fig. 4.10 Moisture Sorption Hysteresis of Peda at 25^{o}C

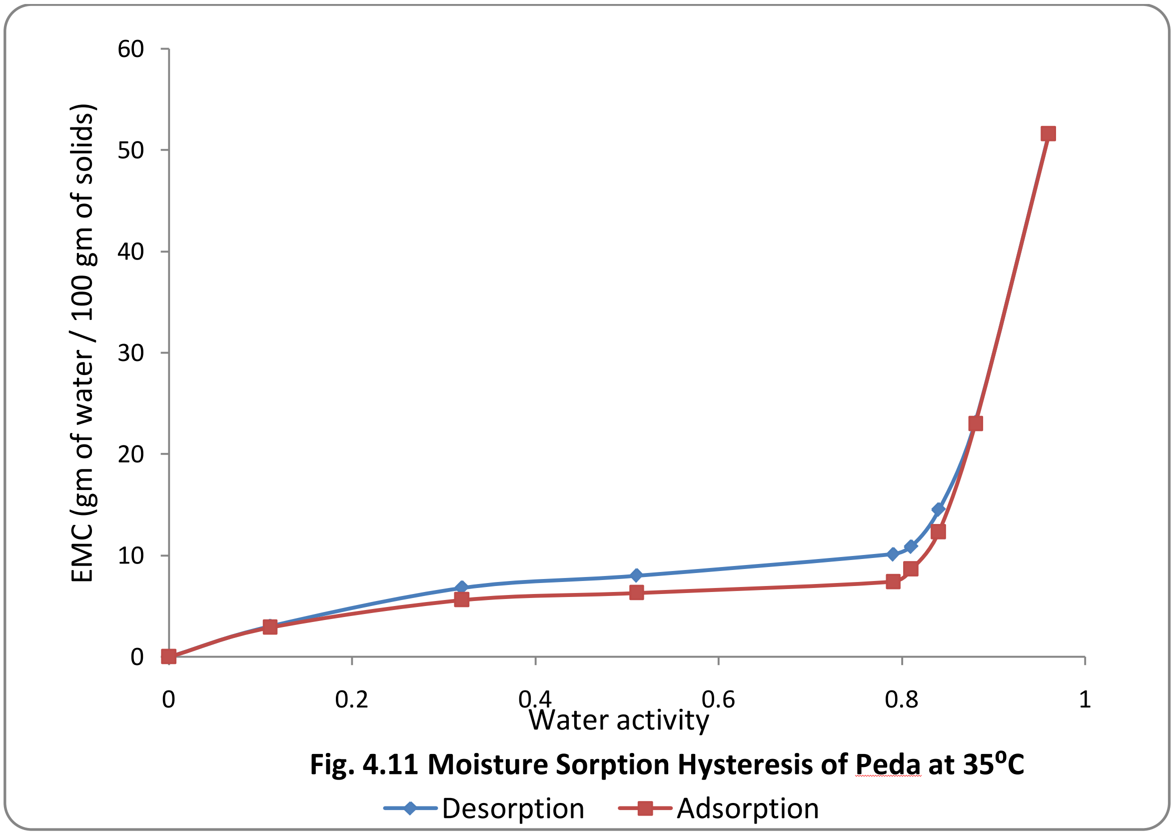

Fig. 4.11 Moisture Sorption Hysteresis of Peda at 35^{o}C

Total hysteresis energy was determined employing the equation 3.23. The Everett and Whitton plots of sorption data on peda 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 60.61 kJ/kg of water at 15^{o}C, 45.63 kJ/kg of water at 25^{o}C and 32.25 kJ/kg of water at 35^{o}C. The effect of temperature was thus found to reduce hysteresis energy.

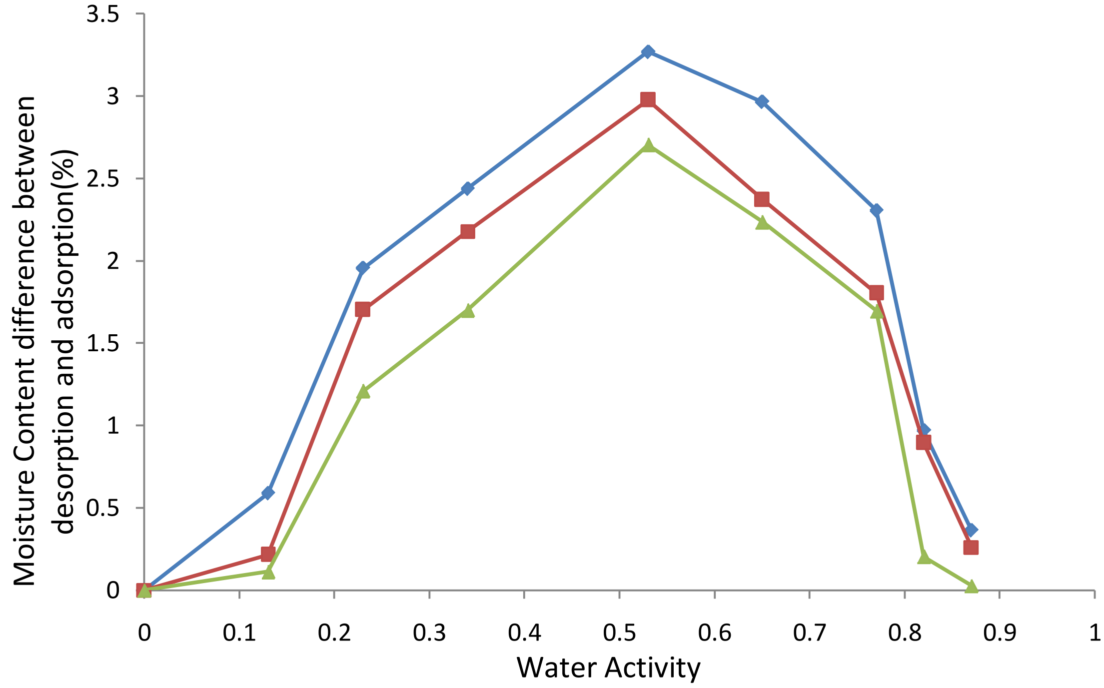

Fig. 4.12 Effect of temperature on derived hysteresis of peda

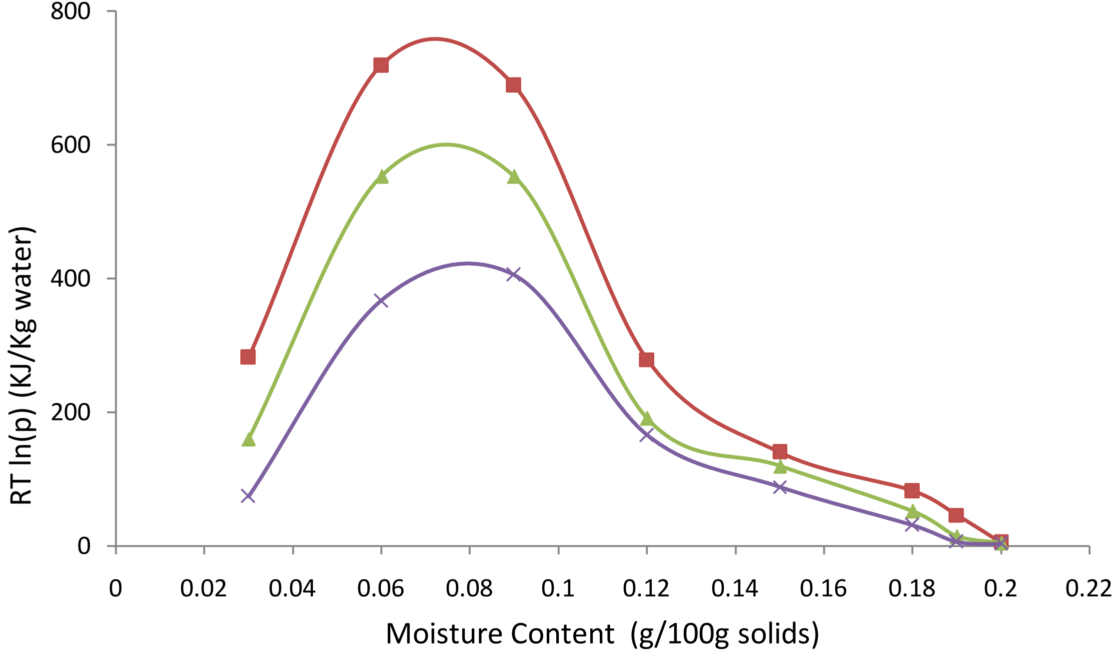

Fig. 4.13 Everett and Whitton Plot for Moisture Sorption Data on Peda at diff. temp.

4.4 MODELING OF ISOTHERM

The experimental data on moisture sorption was fitted to five different two and three parameter models using Eq. 3.8 to 3.12. 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 4.3 for adsorption isotherm and Table 4.4 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 models best described the experimental adsorption data for peda 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 4.87 and 6.18% RMS. This was followed by Modified Mizrahi with % RMS between 6.52 and 14.86. 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 peda at three temperatures 15, 25 and 35^{o}C are presented in Table 4.5 for adsorption and Table 4.6. for desorption. The results show that the adsorbed monolayer moisture content of peda decreased from 5.79 at 15^{o}C to 5.48 g/100g solids at 35^{o}C. Similarly, the desorption monolayer decreased from 6.51 at 15^{o}C to 5.90 g/100g solids at 35^{o}C. 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 4.3 Estimated parameters and root mean square percent error for selected models of adsorption isotherm at different temperatures for peda

Equation	Temperature	Constants			% RMS
		a	b	c	
Halsey	15ºC	1.8529	2.3013	-	9.0118
Oswin		7.6219	0.3187	-	6.8457
Caurie		-3.6891	8.4444	-	11.4530
Modified Mizrahi		-2.6436	-7.9712	10.3548	6.5291
GAB		-0.11	0.1541	0.0139	6.2838
Halsey	25ºC	0.9982	2.11	-	15.2690
Oswin		6.6475	0.348	-	11.7130
Caurie		-4.1827	13.0939	-	15.8986
Modified Mizrahi		-1.5886	-10.6296	12.3867	10.8604
GAB		-0.1034	0.1667	0.0116	4.8712
Halsey	35^0C	1.1595	2.2987	-	16.4489
Oswin		6.0545	0.3084	-	14.4137
Caurie		-3.9692	11.9738	-	18.0382
Modified Mizrahi		-2.05	-7.2971	9.4453	14.8618
GAB		-0.0416	0.1117	0.0256	5.483

Table 4.4 Estimated parameters and root mean square percent error for selected models of desorption isotherm at different temperatures for peda

Equation	Temperature	Constants			% RMS
		a	b	c	
Halsey	15^{0}C	1.9692	2.8311	-	7.6187
Oswin		9.3363	0.2574	-	7.6252
Caurie		-1.8853	0.6846	-	15.606
Modified Mizrahi		-2.9489	-11.187	14.4402	7.5953
GAB		-0.099	0.1477	0.0045	6.1829
Halsey	25^{0}C	1.4661	2.5764	-	7.9267
Oswin		8.7744	0.2975	-	7.4042
Caurie		-1.9606	0.6778	-	14.6618
Modified Mizrahi		-3.6528	-6.8809	10.3712	7.1698
GAB		-0.1078	0.1569	0.0064	6.7896
Halsey	35^{0}C	1.5435	2.9232	-	10.550
Oswin		6.9879	0.2441	-	7.6726
Caurie		-2.2503	0.8646	-	10.602
Modified Mizrahi		-2.9105	-7.1538	10.4613	8.1363
GAB		-0.0854	0.1585	0.0104	6.3082

Table 4.5 Parameter values for GAB model to describe the adsorption isotherm of peda at different temperature

Temperature	GAB Parameters		
	Wo	C	K
15°C	5.79	26.08	0.67
25°C	5.54	18.45	0.65
35°C	5.48	14.67	0.64

Table 4.6 Parameter values for GAB model to describe the desorption isotherm of peda at different temperature

Temperature	GAB Parameters		
	Wo	C	K
15°C	6.51	51.72	0.66
25°C	6.04	38.45	0.67
35°C	5.90	31.24	0.69

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°C. Eq. 3.19 to 3.21 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 peda 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 peda 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 peda.

4.6 EVALUATION OF NET ISOSTERIC HEAT OF SORPTION

The isosteric heat of adsorption and desorption for peda was calculated by applying Clausius- Clapeyron 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 peda 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 peda. 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 11 % dry basis was approached. The maximum isosteric heat of adsorption obtained was 13.72 kJ/mol for desorption and 12.04kJ/mol for adsorption of peda . The maximum enthalpy value indicates the covering of the strongest binding sites and the greater water solid interactions in the peda. Therefore, the water binding in peda prepared from buffalo whole milk was found to be week at moisture content above 11%. 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, 2007). At low moisture levels, the adsorption is mainly at monomolecular layer where the sorption sites are usually active (Iglesias and Chirife, 1976).

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

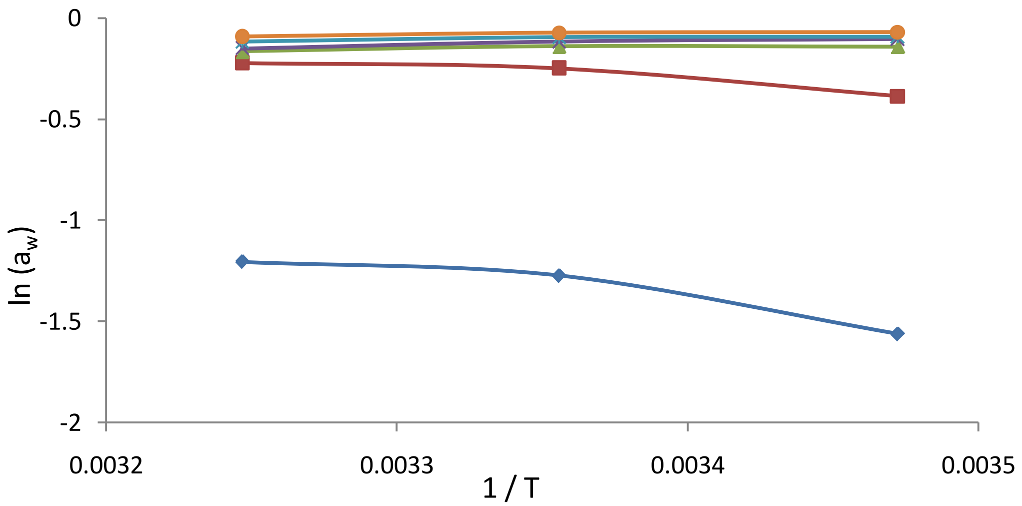

Fig. 4.14 Moisture sorption isosters of adsorption for Peda at different moisture content

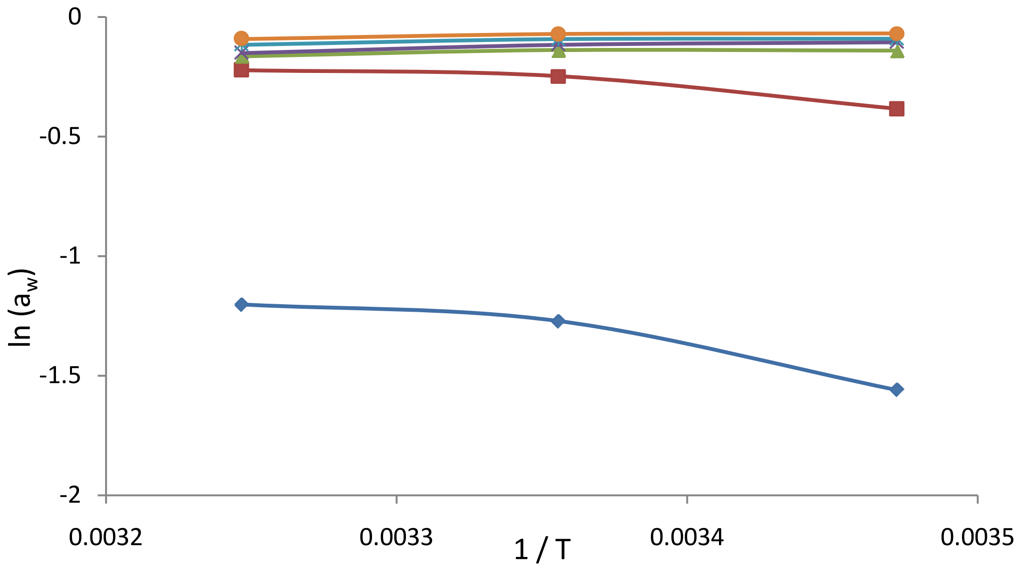

Fig. 4.15 Moisture sorption isosters of desorption for Peda at different moisture content

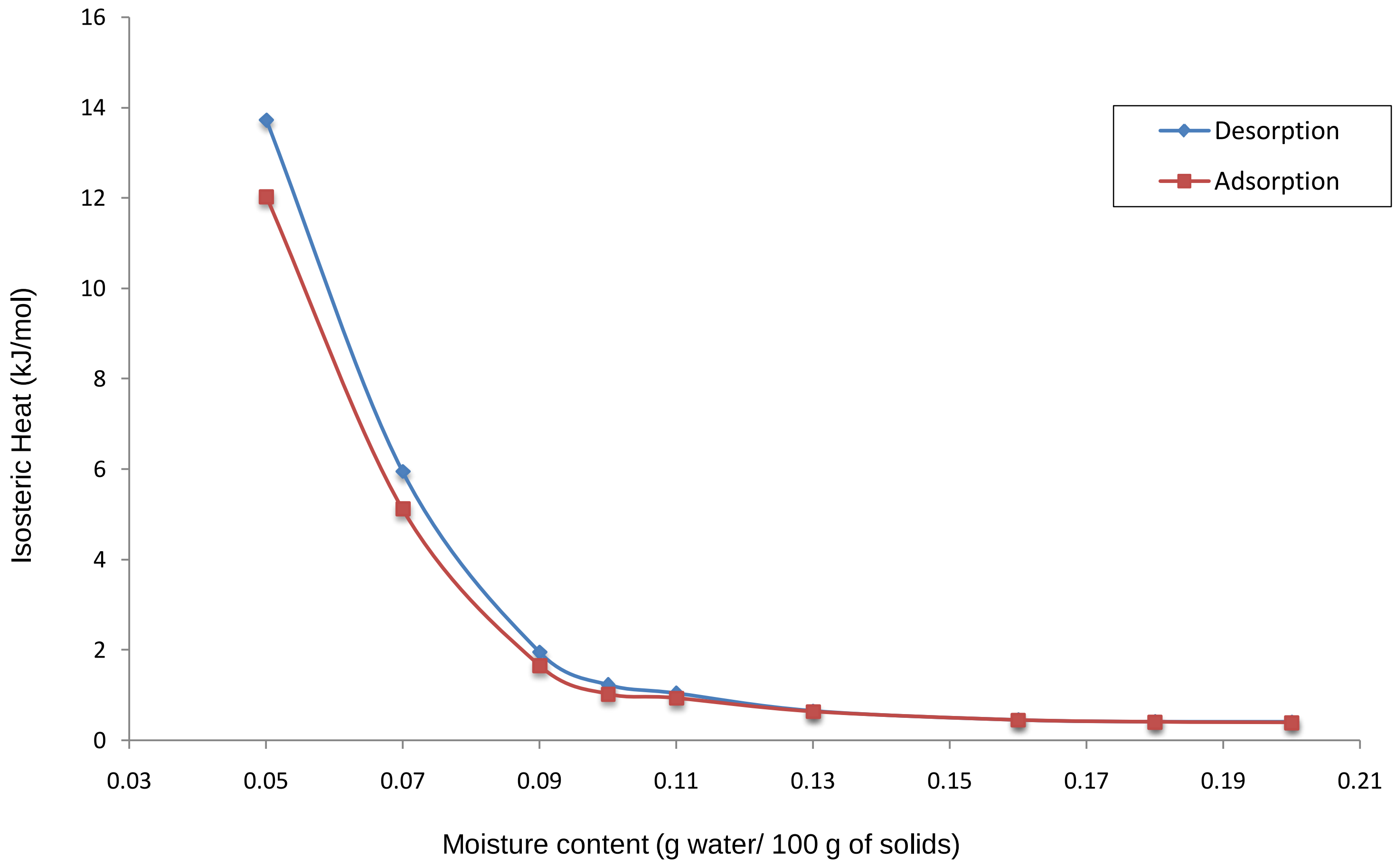

Fig. 4.16 Variation in differential enthalpy (isosteric heat) of adsorption and desorption of peda with moisture content

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 11% 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).

CHAPTER - 5

Summary and Conclusions

SUMMARY AND CONCLUSION

The knowledge of moisture sorption characteristics of food items is valuable in solving food processing and engineering problems such as equipment design, drying and storage conditions as well as prediction of shelf life. Moisture sorption isotherm describes the equilibrium relationship between the moisture content of product and the relative humidity of the surrounding environment at constant temperature. 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 *peda* prepared from buffalo whole milk at 15, 25 and 35ºC by using standard gravimetric method suggested by Wolf *et al.,* (1985). Eight reagent grade salt slurries namely Lithium Chloride, Magnesium Chloride, Magnesium Nitrate, Ammonium Sulphate, Potassium Bromide, Potassium Chloride, Barium Chloride and Potassium Chloride were chosen (Greenspan, 1977) to maintain different water activities. About 1 gm of *peda* sample was equilibrated with the environment of different relative humidity. The desiccators containing samples were placed at 15, 25 and 35ºC. Samples were weighed at interval of two days and equilibrium was judged to have been attaining when difference between three consecutive weighing was less than 0.001gm. Obtained equilibrium moisture content values at different temperature were plotted against the water activity to obtain the moisture sorption isotherm. 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 *peda.*

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:

1. The sorption isotherm of *peda* prepared from buffalo whole milk at different temperature is of type II or sigmoid shape.

2. The hysteresis loop was classified as Type-C according to Everett and Whitton classification.

3. The sorption isotherm exhibited the temperature dependence where the equilibrium moisture content is seen to decrease with increase in temperature at the same water activity.

4. GAB was the best fitted equation for the experimental data of *peda.*

5. Monolayer moisture content decreases with increase in temperature (6.51g/100g solids at 15^0C to 5.90g/100g solids at 35^0C).

6. Heat of sorption of *peda* was found to increase initially and attain a peak value of 13kJ/mol at 5% moisture level and then decreased with increased moisture content.

7. Hysteresis amplitude reduced from 0.303 at 15^oC to 0.253 at 35^oC and total hysteresis units decreased from 1.55 units at 15^oC to 1.25 units at 35^oC.

8. The hysteresis energy reduced from 67.72kJ/kg water at 15^oC to 32.25kJ/kg water at 35^oC.

9. Initial water activity of *peda* at 17% moisture(d.b) was found to be 0.85 at 25^0C.

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