

Moisture Sorption Isotherm of Preconditioned Pressure Parboiled Brown Rice

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Abstract

The pressure parboiling of paddy was carried out at 294.204 kPa for 7 min and preconditioning of brown rice was carried out in fluidized bed dryer at 60-80°C. The moisture sorption isotherms of pressure parboiled preconditioned brown rice at different salt concentrations (0, 2, 3, 3.5 and 4%) were obtained at 20 ± 1°C, 25 ± 1°C, and 30 ± 1°C. The experimental data of sorption isotherm were fitted with some of sorption models (GAB, MGAB, MCPE, MOSE, MHEE, and MHAE models). According to the statistical results, the MGAB model gave the best fit to the experimental sorption data and MHAE model was the least adequate. Sorption isotherm data were used to determine the some thermodynamic functions. The net isosteric heat of sorption was determined from the best fitting equation using the Clausius-Calpeyron equation. The net isosteric heat of sorption decreased with increasing moisture content and increased with increasing salt concentration same trend was observed in entropy of sorption. The spreading pressure increased with increasing water activity and salt concentration and decreased with increasing temperature. The net integral enthalpy decreased with increasing moisture content and increased with increasing salt concentration and reverse trend was observed in integral entropy.

Keywords: Brown rice; Equilibrium moisture content; Pressure parboiling; Sorption isotherms; Spreading pressure

Notation

A,B,C :	Model constants
A_m :	Area of water molecule, $1.06 \times 10^{-19} \text{ m}^2$
a,b,c :	Constants
a_w :	Water activity
°C :	Degree Celsius
CG, k_G :	GAB model constants
K :	Boltzmann's constant, $1.38 \times 10^{-23} \text{ J/K}$
K :	Net isosteric heat constant
M_o :	Monolayer moisture content, kg water/ kg dry solids
M_e :	Equilibrium moisture content, kg water/ kg dry solids
M_r :	Constant
R :	Universal gas constant, 8.314 kJ/mol K
R^2 :	Coefficient of determination
T :	Temperature, K
Q_{st} :	Net isosteric heat of sorption, kJ/mol
Q_o :	Constant, kJ/mol
Q_{eq} :	Net integral enthalpy, kJ/mol
ΔS_{eq} :	Net integral entropy, kJ/mol K
ΔS :	Entropy of sorption, J/mol K
\emptyset :	Spreading pressure (J/m ²)

Introduction

Rice ranks first in terms of global production (603 million tonnes) and used as a staple food for approximately 400 million people in the developing countries [1]. India exports 5% of the produced rice to

the international market and compete with Thailand, Vietnam, and Pakistan. About 10% of the production of paddy is converted to three rice products, namely, puffed rice, popped rice and flaked rice [2-4]. Among the rice based breakfast cereals, puffed rice is largely demanded product for centuries in India because of its lightness and crispness. When grains such as rice, paddy, corn, gram etc. are heated, vapour pressure of water inside the grain increases. At a certain temperature and after certain duration of time the vapour pressure becomes high which causes expansion of the grain and the process is called puffing [5,6].

Preconditioning of rice is the most critical factor for obtaining highly expanded smooth-surface puffed rice [7]. The process comprises of uniform and slow heating of moisture-salt-conditioned parboiled rice with continuous turning until optimum moisture content of puffing (10% w.b.) is attained. Non uniform heating of grain severely impairs the quality of product with less expansion ratio in addition to rough and blistered surface. Further, puffing efficiency for rice grain depends on several factors, including the nature and concentration of salts diffused into the kernel.

Water activity of food material is determined as the ratio of vapour pressure of water in the food to vapour pressure of pure water at the same temperature. Many food deterioration reactions and the growth of important microorganisms depend on the water activity of the food and water activity is thus an important parameter to predict food stability. In order to determine the storage conditions, it is necessary to know the relationship between the equilibrium moisture content

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(EMC) in the rice and equilibrium relative humidity of the aeration air at a given temperature. This relationship is described by the sorption isotherm equations [8]. The knowledge of the EMC of rice at several temperatures would allow specifying the storage conditions of rice.

Thermodynamic properties that describe the relationship between water and food are helpful in evaluating the energy requirements in concentration and drying processes and in predicting optimal storage conditions for maximum stability of dry foods. In addition, the evaluation of several thermodynamics properties (enthalpy, entropy, Gibbs free-energy, etc.) is important in the design and optimization of dryers. The isosteric heat of sorption gives a measure of the water-solid binding strength [9]. Knowledge of the differential heat of sorption is useful for designing drying equipment and the understanding of the state of water on food surface [10]. Net integral enthalpy and entropy are used to explain the modes of moisture sorption by foods.

Studies on the sorption behaviour of different varieties of rice were carried out by different authors, jasmine rice crackers, rice [10-13], rough rice [14-16], rice kernel components [17], but to the best of my knowledge, no study has been reported on the moisture sorption of preconditioned pressure parboiled brown rice at different salt concentrations. Moisture content of preconditioned rice is the most critical factor for achieving the best quality expanded product. After preconditioning immediately rice has to be puffed otherwise rice should store in moisture proof packaging material to maintain constant moisture content of preconditioned rice. During storage absorption of moisture may deteriorate the puffing quality. Data on MSI of such preconditioned rice will help to evaluate energy required for dehydration and design of packaging systems for storage. Considering these aspects and identifying the existing knowledge gap, the present study has been undertaken with the following objectives.

- To determine the effect of salt concentration and temperature on the moisture sorption isotherm of preconditioned brown rice.
- To evaluate several models and compare their goodness of fit.
- To determine thermodynamic properties and effect of salt concentration on thermodynamic properties such as isosteric heat of sorption, differential enthalpy and entropy, spreading pressure and integral enthalpy and entropy.

Materials and Methods

Experimental procedure

IR 1010 variety of pressure parboiled brown rice were collected from local rice mill located at Balichak, West Bengal, India. The paddy was soaked for nearly 8 min in cold water and then steamed under pressure at 294.204 kPa for 7 min after that paddy was dried until the moisture content of paddy was reached to 12-14% (w.b.). After reaching the optimum moisture content the paddy was milled by using rubber roll sheller. 150 ml of water per kg of rice was mixed with salt (NaCl) at pre-determined rate so as to arrive its concentration in the final dried mass 0-4% (w/w). This was followed by tempering for about 6 to 8 hours to facilitate diffusion of both water and salt into the kernel. Preconditioning was carried out using hot air at specific temperature (60-80°C) using fluidized-bed dryer (Lab dryer, Basic technology Pvt. Ltd, India). This process was continued until the moisture content reaches around 10% (w.b.). To maintain different moisture contents of sample, preconditioned sample was kept in desiccators containing water to maintain moisture content more than 10% and silica gel to maintain moisture content lower than 10%. The moisture contents of

these samples were checked frequently to obtain required moisture content. After attaining desired moisture contents water activity of pre-conditioned rice samples having different moisture contents were noted at different room temperatures ($20 \pm 1^\circ\text{C}$, $25 \pm 1^\circ\text{C}$, and $30 \pm 1^\circ\text{C}$) using water activity meter (Rotronic, HygroLab C1).

Data analysis

Isotherm models: Experimental moisture sorption data can be described by many sorption models but for this study six isotherm equations were chosen to fit experimental sorption data these are shown in Table 1. Non-linear regression analysis was carried to find out model constants. The extent of fitting of models was evaluated and compared based on three statistical criteria namely coefficient of determination (R^2), Root mean square error (RMSE), and reduced- χ^2 .

Root mean square error

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (X_{\text{obs},i} - X_{\text{model},i})^2}{n}} \quad (1)$$

$$\text{Reduced } \chi^2 = \frac{1}{\text{d.f}} \sum \frac{(X_{\text{obs}} - X_{\text{model}})^2}{\sigma^2} \quad (2)$$

Where X_{obs} is observed values and X_{model} is predicted value.

In general, low values of the correlation coefficient, high values of reduced- χ^2 , and RMSE, means that the model is not able to explain the variation in the experimental data. It is also evident that a single statistical parameter cannot be used to select the best model and the model must always be assessed based on multiple statistical criteria.

Net isosteric heat of sorption: The net isosteric heat of sorption (Q_{st}) (differential) is defined as the total heat of sorption in the food minus the heat of vaporisation of water at the system temperature [18]. This thermal property can be determined from calorimetric measurements or more easily from moisture sorption data. The usual procedure to evaluate isosteric heat of sorption from moisture isotherm is based on a Clausius-Clapeyron equation derived equation [19].

$$\ln a_w = -\left(\frac{Q_{\text{st}}}{R}\right)\left(\frac{1}{T}\right) + k \quad (3)$$

Model	Mathematical expression
MGAB	$M_e = \frac{A \cdot B \cdot a_w \cdot \frac{C}{T}}{(1 - B \cdot a_w) [1 - B \cdot a_w + a_w \cdot B \cdot (\frac{C}{T})]}$
MCPE	$M_e = -\frac{1}{C} \ln \left[-\left(\frac{T+B}{A}\right) \ln a_w \right]$
MOSE	$M_e = (A + B \cdot T) \cdot \left(\frac{a_w}{1 - a_w}\right)^{\frac{1}{C}}$
MHEE	$M_e = \left[\frac{\ln(1 - a_w)}{A \cdot (T + B)} \right]^{\frac{1}{C}}$
MHAE	$M_e = \left[\frac{\exp(A + B \cdot T)}{\ln a_w} \right]^{\frac{1}{C}}$
GAB	$m = \frac{m_o \cdot C_G \cdot k_G \cdot a_w}{(1 - k_G \cdot a_w) (1 - k_G \cdot a_w + k_G \cdot a_w \cdot C_G)}$

Table 1: Mathematical models used to fit experimental data of preconditioned brown rice.

Where, R is universal gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$), T is temperature in K and k is integral constant. The net isosteric heat of sorption is obtained from the slope of the graph representing $\ln a_w$ versus $(1/T)$ at a particular equilibrium moisture content. This is carried out for several equilibrium moisture content determined by the best fitting sorption model. The correlations between Q_{st} and M_e have been reported by various authors [14,20,21].

$$Q_{st} = Q_0 \exp\left(\frac{-M_e}{M_r}\right) \quad (4)$$

$$Q_{st} = \left(\frac{a \cdot M_e^b}{c + M_e^d}\right) \quad (5)$$

Differential entropy: The differential entropy (ΔS) of sorption of water at each equilibrium moisture content was obtained by fitting to Equation (5) for various equilibrium moisture contents calculated from the best-fitting equation [22,23].

$$-\ln a_w = \frac{Q_{st}}{RT} - \frac{\Delta S}{R} \quad (6)$$

By plotting $\ln a_w$ versus $1/T$, for given equilibrium moisture content, ΔS was determined from the intercept ($\Delta S/R$). Many authors discuss about the relationship between ΔS and equilibrium moisture content McMinn and Magee [9] gave a power law relationship.

Spreading pressure: It is also called as surface potential, it is the force applied in the surface plane perpendicular to each unit length of edge to keep the surface from spreading. It represents the surface excess free energy [24]. It acts as a second pressure [12] and results in increase in surface tension on bare sorption sites due to the sorbed molecules on them [25]. It was calculated using an analytical procedure

$$\phi = \frac{kT}{A_m} \int_0^{a_w} \frac{m}{a_w m_0} da_w \quad (7)$$

Where k is Boltzman constant (1.38×10^{-23} , J/K); A_m is the area

that occupies one single water molecule at monolayer ($1.06 \times 10^{-19} \text{ m}^2$). Combine the GAB equation with the above equation mathematically expressed the ϕ in the form of GAB equation [26].

$$\phi = \frac{kT}{A_m} \ln \left[\frac{1 - k_G a_w + k_G C_G a_w}{1 - k_G a_w} \right] \quad (8)$$

Net integral enthalpy and entropy: The net integral enthalpy (q_{eq}) represents the total energy available to do the work. It gives an indication of the binding strength of water molecules to the solid. The net integral enthalpy is calculated in a similar manner to the isosteric heat but at constant spreading pressure. A plot of $\ln a_w$ versus $1/T$ at a constant spreading pressure (ϕ) gives the net integral enthalpy from the slope [19].

$$q_{eq} = -R \left[\frac{d(\ln a_w)}{d\frac{1}{T}} \right] \phi \quad (9)$$

Net integral entropy (ΔS_{eq}) indicates the degree of disorder and randomness of motion of water molecules [27], it is calculated by using the following equation.

$$\Delta S_{eq} = \frac{-q_{eq}}{T} - R \ln(a_w)^* \quad (10)$$

Where $(a_w)^*$ is the geometric mean water activity obtained at a constant spreading pressure at different temperatures [9].

Results and Discussions

Sorption curves

The moisture sorption isotherms of preconditioned pressure parboiled rice at salt different concentrations at $20 \pm 1^\circ\text{C}$, $25 \pm 1^\circ\text{C}$ and $30 \pm 1^\circ\text{C}$ are shown in Figure 1. The results reveal that the water activity

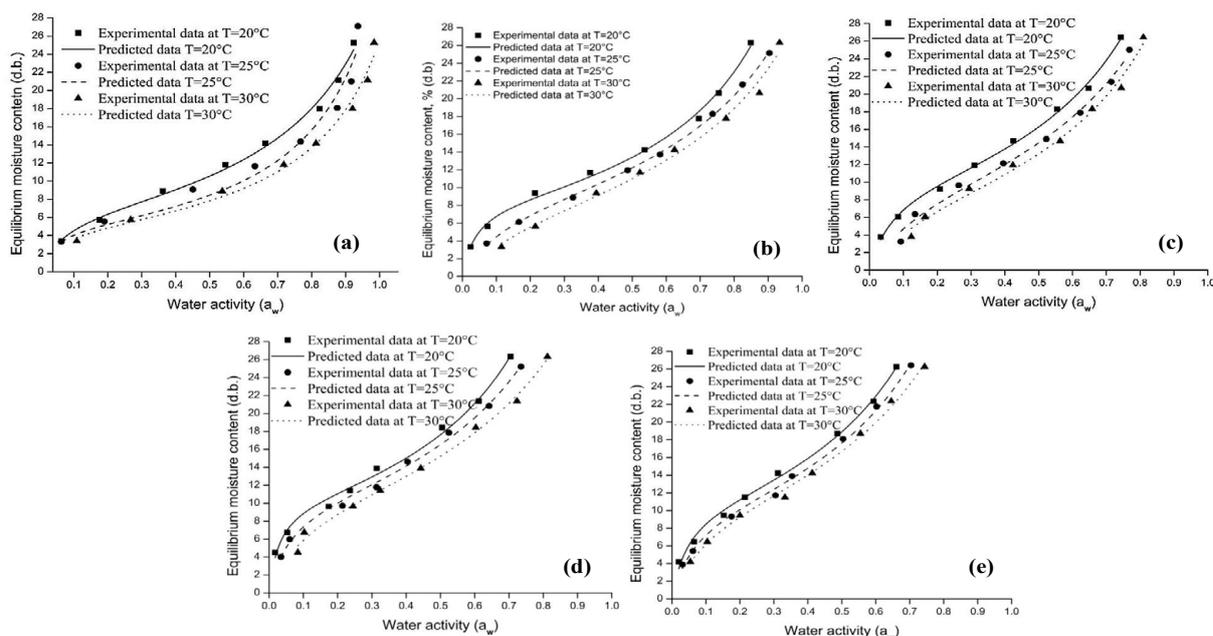


Figure 1: Effect of temperature on moisture sorption isotherm of pre conditioned pressure parboiled brown rice at (a) 0% salt, (b) 2% salt, (c) 3% salt, (d) 3.5% salt and (e) 4% salt.

increased with increasing EMC at constant temperature. These changes in EMC are due to the inability of the food to maintain vapour pressure at unity with decreasing moisture content. As moisture content decreased, moisture in the food tend to show a lower vapour pressure, acting as if in solution, changing with atmospheric humidity. These changes in vapour pressure in the food with atmospheric humidity result in the characteristic sigmoid shape of water sorption isotherms [10]. The isotherm presented a sigmoid shape (Type II according to BET classification) which is common for most of the hygroscopic foods. Sorptive behaviour depends on the temperature, it is decreasing with increasing temperature due to the activation of water molecules, at higher temperatures causes them to break away from the water binding sites, thus lowering the equilibrium moisture content [9] these results were compared with various researchers [14,15,28-30]. Effect of salt concentration on moisture sorption isotherm of preconditioned brown rice sample is shown in Figure 2. Where the water activity is seen to decreases with increasing salt concentration due to the ability of sodium and chloride ions to associate with water molecules [31,32]. These results are compared with the effect of salt and glucose concentration on water activity is explained by Martin Chaplin [33].

Fitting sorption models to experimental sorption data

The model coefficients and corresponding statistical results for the sorption models are listed in Tables 2-4. The goodness of fit was evaluated by using higher values of R^2 and lowest values of RMSE and reduced- χ^2 . The average coefficients of determination (R^2) in all cases were greater than 0.940, the $RMSE \leq 2.152$ and the Reduced- $\chi^2 \leq 4.629$. Among six models MGAB, MHEE and MOSE models gave better curve fitting compared to other models at all temperatures throughout the entire range of water activity. Least RMSE and reduced- χ^2 values were

obtained in case of GAB model and maximum RMSE and reduced- χ^2 values were obtained in case of MHAE model over the temperature and salt concentration range. MGAB model gave the least value of RMSE and reduced- χ^2 and higher value of R^2 was considered the best model in case of all samples and MHAE gave the poor fitting results. The goodness of fit has been reported by several authors studying sorption behaviour of different food materials, GAB, BET and Halsey models [34] for blue berry, GAB model [21] for dent corn, GAB model [35] for capsicum, Modified Oswin [36] for millet, Strohman-Yoerger equation [13] for rice and Modified GAB [14] for rice.

Net isosteric heat of sorption and sorption entropy

Net isosteric heat of sorption and sorption entropy of preconditioned brown rice were determined by using Clausius-Clapeyron equation (Equation 3) to the experimental equilibrium isotherm data. The isosteric heat of sorption is strong moisture dependent. The net isosteric heat of sorption decreased with increasing moisture content is shown in Figure 3. It is due to the fact that sorption initially occurs on the most active primary sites giving rise to higher exothermic interaction energies than those released when these sites become occupied [21]. Similar trends have been reported for isosteric heat of sorption of jasmine rice crackers [11], rough rice [14], rice [10,30], potato [37]. It is depicted from Figure 3, Isosteric heat of sorption increased with increasing salt concentration. This confirms the fact that at higher salt concentrations, the strength of water binding increases. Most of the authors described the relation between Q_{st} and M_e the model constants and stastical data of models suggested by Tsami et al. [38] and Kechau and Maalej [20] were shown in Table 5, from these results, it can be revealed that Kechau and Maalej [20] model gave the best relationship between Q_{st} and M_e . Some more others express relations between Q_{st}

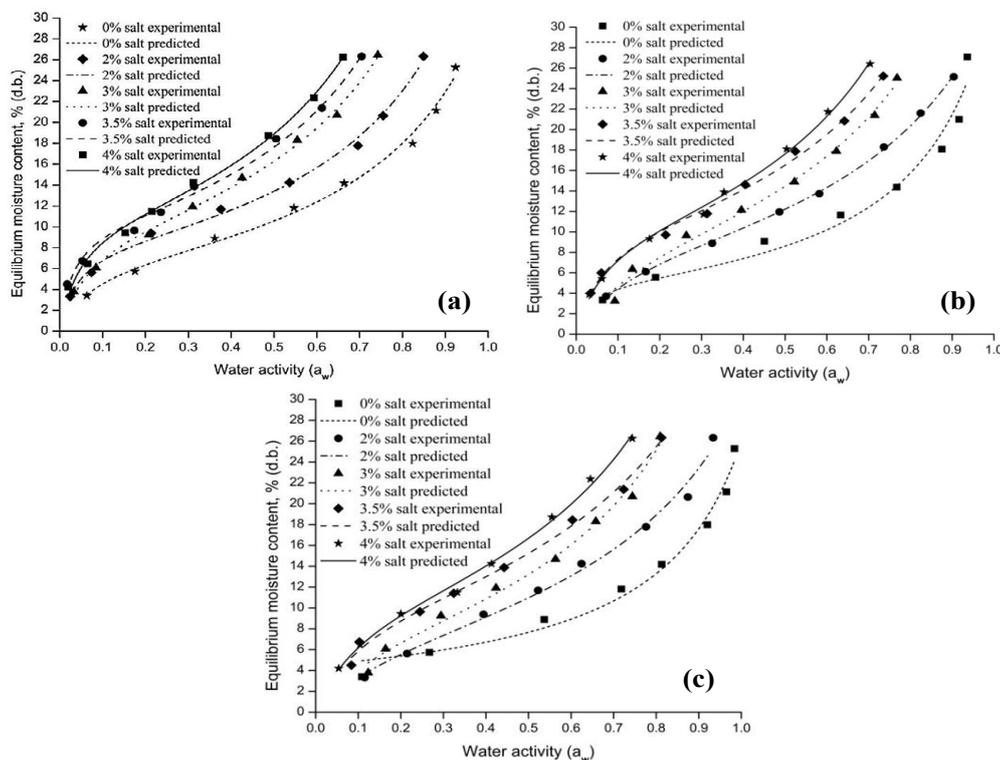


Figure 2: Effect of salt concentration on moisture sorption isotherm of pre conditioned pressure parboiled rice at (a) $20 \pm 1^\circ\text{C}$, (b) $25 \pm 1^\circ\text{C}$ and (c) $30 \pm 1^\circ\text{C}$.

Models		0% salt	2% salt	3% salt	3.5% salt	4% salt
MGAB	A	7.037	8.403	10.153	10.197	10.911
	B	0.778	0.802	0.844	0.880	0.901
	C	345.825	646.899	346.239	782.635	482.052
	Reduced - χ^2	0.490	0.294	0.216	0.457	0.325
	R ²	0.994	0.997	0.997	0.994	0.996
	RMSE	0.700	0.542	0.465	0.676	0.570
MCPE	A	454.796	501.715	431.728	529.803	436.290
	B	81.135	69.692	72.185	68.967	62.001
	C	0.167	0.144	0.111	0.115	0.103
	Reduced - χ^2	0.436	1.292	1.079	1.352	1.037
	R ²	0.995	0.985	0.987	0.983	0.988
	RMSE	0.660	1.137	1.039	1.163	1.018
MOSE	A	-4.178	12.300	13.774	15.221	15.254
	B	0.741	0.075	0.139	0.161	0.213
	C	2.868	2.759	2.332	2.618	2.414
	Reduced - χ^2	0.319	0.365	0.169	0.375	0.163
	R ²	0.996	0.996	0.998	0.995	0.998
	RMSE	0.565	0.604	0.411	0.613	0.404
MHAE	A($\times 10^{-5}$)	7.097	4.096	4.527	2.403	2.839
	B	142.230	71.128	81.860	44.102	51.351
	C	1.700	1.948	1.762	2.075	1.949
	Reduced - χ^2	0.719	1.890	0.815	1.340	0.717
	R ²	0.991	0.978	0.990	0.983	0.992
	RMSE	0.848	1.375	0.903	1.158	0.847
MGAB	A	6.945	6.647	6.138	6.323	6.092
	B	-0.099	-0.103	-0.113	-0.104	-0.110
	C	2.302	1.945	1.543	1.611	1.451
	Reduced - χ^2	1.959	1.535	1.378	0.859	1.041
	R ²	0.976	0.982	0.983	0.989	0.988
	RMSE	1.400	1.239	1.174	0.927	1.020
GAB	m ₀	0.070	0.082	0.100	0.102	0.106
	c	17.291	17.311	24.100	39.130	39.132
	k	0.778	0.811	0.849	0.880	0.916
	Reduced - $\chi^2(\times 10^{-5})$	4.904	16.580	5.716	4.574	9.239
	R ²	0.994	0.980	0.993	0.994	0.989
	RMSE	0.007	0.013	0.008	0.007	0.010

Table 2: Estimated parameters of preconditioned pressure parboiled rice at different salt concentration solutions for different isotherm models at 20°C.

and Me for different food materials, power function [9] for potato, exponential function for onions and exponential form [17] for rough rice.

The entropy of sorption of preconditioned pressure parboiled brown rice as a function of moisture content is shown in Figure 4, from this figure it can be observed that entropy of sorption decreased with increasing moisture content, similar trends have been reported for differential entropy of starch powders [39], pepper [40], crushed chillies [8] but for rice stored under controlled humidity chamber reported that sorption entropy decreased with increasing moisture content in desorption process but in adsorption process increased up to certain moisture content later it decreased with increasing moisture content [10]. Differential entropy increased with increasing salt concentration (Figure 4) from this we can reveal that number of sorption sites were more at higher salt concentration at a specific energy level. The ΔS versus M_e results are adequately represented by an exponential relation as represented by the equation

0% salt $\Delta S=0.307e^{-0.134M_e}$ R² = 0.994

2% salt $\Delta S=0.919e^{-0.214M_e}$ R² = 0.978

3% salt $\Delta S=0.392e^{-0.130M_e}$ R² = 0.993

3.5% salt $\Delta S=0.504e^{-0.156M_e}$ R² = 0.957

4% salt $\Delta S=0.345e^{-0.110M_e}$ R² = 0.984

Many authors describe a relation between ΔS and M_e power function [9] for potato, exponential form [26] for Mexican mennonite-style cheese and exponential [39] for the starch powders.

Net integral enthalpy and entropy

Net integral enthalpy given by Equation 9, the experimental sorption data were first represented in the form of spreading pressure isotherm. Spreading pressure values were calculated using Eq. 8 the constants C_G and K_G were determined from the GAB equation (Table 1). Spreading pressure increased with increasing water activity and salt

Models		0% salt	2% salt	3% salt	3.5% salt	4% salt
MGAB	A	5.100	9.005	10.285	10.510	10.724
	B	0.849	0.732	0.796	0.814	0.871
	C	700.000	267.807	208.718	506.351	413.963
	Reduced- χ^2	2.843	0.052	0.555	0.288	0.247
	R ²	0.969	0.999	0.993	0.996	0.997
	RMSE	1.686	0.228	0.745	0.537	0.497
MCPE	A	443.457	455.305	389.890	99.419	420.237
	B	83.842	78.834	82.662	-5.570	65.252
	C	0.175	0.148	0.110	0.116	0.103
	Reduced- χ^2	3.857	0.170	0.823	0.679	1.252
	R ²	0.957	0.998	0.989	0.991	0.986
	RMSE	1.964	0.413	0.907	0.824	1.119
MOSE	A	-7.394	11.221	12.368	14.113	13.978
	B	0.664	0.029	0.075	0.105	0.159
	C	2.669	2.821	2.145	2.485	2.237
	Reduced- χ^2	1.536	1.111	0.799	0.195	0.137
	R ²	0.983	0.986	0.990	0.997	0.998
	RMSE	1.239	1.054	0.894	0.442	0.370
MHAE	A($\times 10^{-5}$)	10.140	6.153	6.664	3.307	4.054
	B	213.857	119.535	133.194	68.685	83.617
	C	1.492	1.727	1.550	1.897	1.733
	Reduced- χ^2	4.115	0.138	0.886	0.612	0.706
	R ²	0.954	0.998	0.989	0.992	0.992
	RMSE	2.029	0.371	0.941	0.782	0.840
MGAB	A	6.916	7.136	6.235	6.502	6.244
	B	-0.100	-0.082	-0.107	-0.096	-0.102
	C	2.193	2.235	1.513	1.619	1.430
	Reduced- χ^2	1.819	3.730	2.116	1.672	1.413
	R ²	0.980	0.953	0.973	0.978	0.984
	RMSE	1.349	1.931	1.455	1.293	1.189
GAB	m ₀	0.042	0.091	0.100	0.109	0.107
	c	7.827	9.349	10.712	16.559	20.254
	k	0.883	0.728	0.806	0.798	0.874
	Reduced - $\chi^2(\times 10^{-5})$	94.920	1.062	8.350	3.684	4.194
	R ²	0.895	0.999	0.989	0.995	0.995
	RMSE	0.031	0.003	0.009	0.006	0.006

Table 3: Estimated parameters of preconditioned pressure parboiled rice at different salt concentration solutions for different isotherm models at 25°C.

Models		0% salt	2% salt	3% salt	3.5% salt	4% salt
MGAB	A	4.966	8.825	9.322	10.881	11.150
	B	0.807	0.723	0.817	0.744	0.812
	C	688.789	204.869	225.580	370.829	351.994
	Reduced $-\chi^2$	0.975	0.769	0.734	0.374	0.319
	R ²	0.988	0.991	0.991	0.995	0.996
	RMSE	0.987	0.877	0.857	0.612	0.565
MCPE	A	495.111	434.463	377.374	76.310	410.615
	B	72.002	83.955	86.273	-13.109	67.366
	C	0.228	0.154	0.110	0.120	0.104
	Reduced $-\chi^2$	0.076	0.401	1.169	0.465	0.847
	R ²	0.999	0.995	0.986	0.994	0.990
	RMSE	0.275	0.633	1.081	0.682	0.921
MOSE	A	-10.107	10.470	11.532	12.972	12.828
	B	0.630	0.009	0.051	0.066	0.128
	C	3.770	2.870	2.092	2.548	2.245
	Reduced $-\chi^2$	1.530	1.971	0.818	0.581	0.342
	R ²	0.981	0.977	0.990	0.993	0.996
	RMSE	1.237	1.404	0.904	0.762	0.585
MHEE	A($\times 10^{-5}$)	8.955	7.544	8.033	3.996	4.527
	B	187.440	156.616	170.688	89.839	98.821
	C	1.675	1.620	1.437	1.806	1.675
	Reduced $-\chi^2$	0.307	0.472	1.095	0.556	0.560
	R ²	0.996	0.994	0.987	0.993	0.993
	RMSE	0.554	0.687	1.046	0.746	0.749
MHAE	A	8.427	7.462	6.470	6.930	6.560
	B	-0.050	-0.074	-0.098	-0.082	-0.091
	C	3.372	2.387	1.550	1.826	1.518
	Reduced $-\chi^2$	3.609	4.629	1.944	2.327	1.864
	R ²	0.955	0.945	0.976	0.971	0.978
	RMSE	1.900	2.152	1.394	1.526	1.365
GAB	m ₀	0.049	0.087	0.093	0.109	0.111
	c	6.742	7.219	7.519	11.733	12.361
	k	0.810	0.727	0.817	0.744	0.812
	Reduced $-\chi^2(\times 10^{-5})$	30.358	7.728	7.344	3.974	3.376
	R ²	0.962	0.991	0.991	0.995	0.996
	RMSE	0.017	0.009	0.009	0.006	0.006

Table 4: Estimated parameters of preconditioned pressure parboiled rice at different salt concentration solutions for different isotherm models at 30°C.

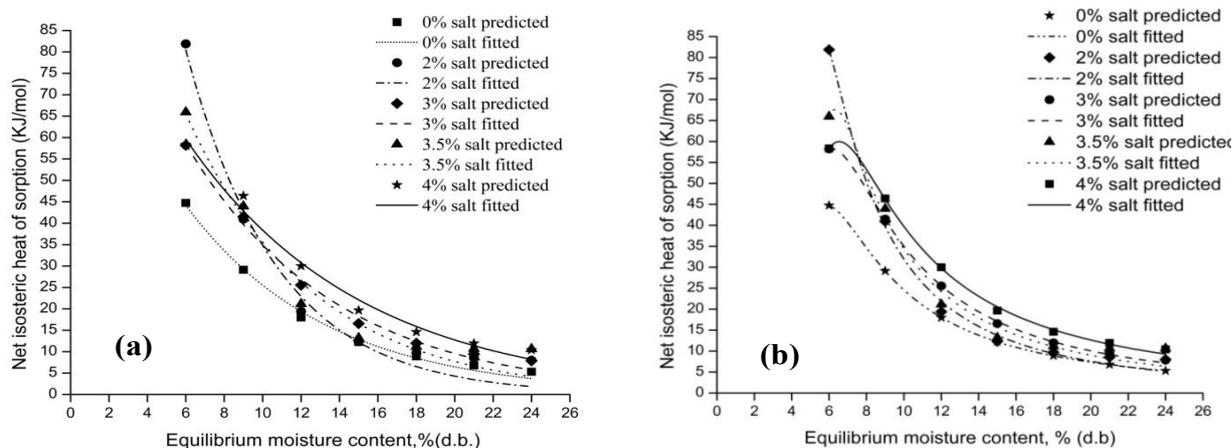


Figure 3: Net isosteric heat of sorption of preconditioned pressure parboiled brown rice at different salt concentrations fitted with (a) Tsami et al. model (b) Kechau and Maalej model.

Models		0% salt	2% salt	3% salt	3.5% salt	4% salt
Kechau and Maalej [24]	a	1470.814	3830.65	2625.3	2949.984	2044.665
	b	3.884	6.552	3.371	8.539	4.162
	c	9614.959	675433.616	7235.502	56946200	24450.6
	d	5.652	8.63	5.228	10.471	5.859
	Reduced- χ^2	0.003	6.907	0.309	14.766	0.833
	R ²	1	0.995	1	0.984	0.999
	RMSE	0.058	2.628	0.555	3.843	0.913
Tsami et al. [44]	Q ₀	100.769	282.688	127.133	164.095	115.55
	M _r	7.282	4.775	7.734	6.542	9.072
	Reduced- χ^2	1.326	18.354	2.817	20.404	5.551
	R ²	0.995	0.979	0.993	0.963	0.987
	RMSE	1.151	4.284	1.678	4.517	2.356

Table 5: Fitted parameters of net isosteric heat of sorption versus equilibrium moisture content for different models.

aw	0% salt			2% salt			3% salt			3.5% salt			4% salt		
	20°C	25°C	30°C	20°C	25°C	30°C	20°C	25°C	30°C	20°C	25°C	30°C	20°C	25°C	30°C
0.100	0.034	0.022	0.018	0.035	0.021	0.018	0.045	0.026	0.020	0.060	0.035	0.026	0.061	0.042	0.029
0.200	0.055	0.038	0.033	0.056	0.037	0.032	0.068	0.043	0.036	0.085	0.055	0.044	0.087	0.065	0.048
0.300	0.070	0.052	0.046	0.072	0.050	0.044	0.085	0.058	0.049	0.103	0.071	0.058	0.105	0.082	0.063
0.400	0.083	0.065	0.057	0.085	0.061	0.054	0.099	0.070	0.061	0.118	0.084	0.071	0.121	0.096	0.077
0.500	0.095	0.077	0.068	0.097	0.072	0.065	0.112	0.082	0.072	0.132	0.096	0.082	0.135	0.109	0.089
0.600	0.106	0.089	0.079	0.109	0.082	0.074	0.124	0.093	0.083	0.145	0.108	0.093	0.148	0.122	0.100
0.700	0.117	0.102	0.090	0.121	0.092	0.084	0.137	0.105	0.095	0.159	0.120	0.103	0.163	0.136	0.112
0.800	0.129	0.116	0.102	0.133	0.102	0.095	0.151	0.117	0.107	0.173	0.132	0.115	0.179	0.150	0.125
0.900	0.142	0.134	0.117	0.148	0.114	0.106	0.167	0.131	0.122	0.191	0.146	0.127	0.199	0.168	0.140

Table 6: Effect of temperature and salt concentration on spreading pressure of pre conditioned brown rice at constant water activity.

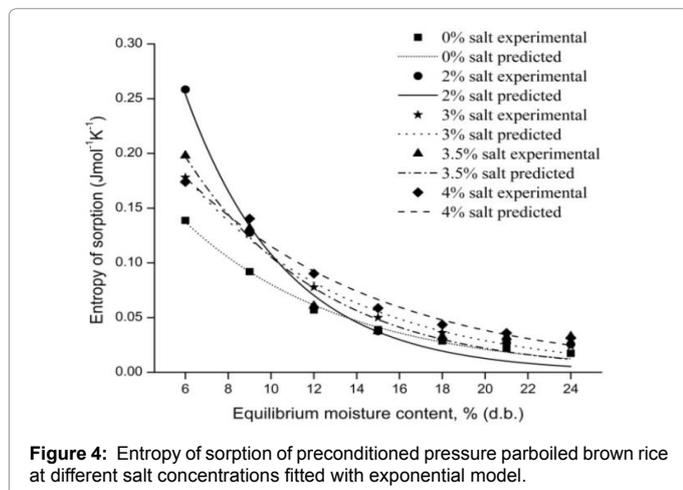


Figure 4: Entropy of sorption of preconditioned pressure parboiled brown rice at different salt concentrations fitted with exponential model.

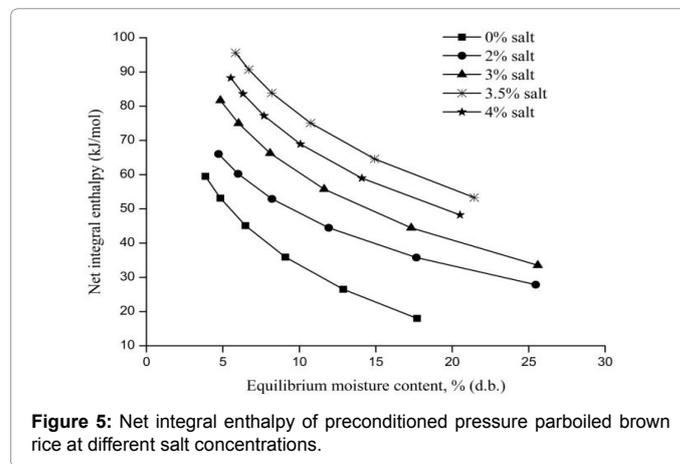


Figure 5: Net integral enthalpy of preconditioned pressure parboiled brown rice at different salt concentrations.

concentration and decreased with increasing temperature at a specific water activity (Table 6). The trends of spreading pressure with respect to temperature and water activity are comparable with [41] starchy materials [42], cereal grains [10], rice and [39] starch powders.

Effect of moisture content on net integral enthalpy of preconditioned pressure parboiled brown rice is shown in Figure 5. This graph clearly shows that net integral enthalpy decreased with increasing moisture content. At low moisture contents, water is adsorbed on the most accessible locations on the exterior surface of the solid. The net integral enthalpy then starts to decline as less favourable locations are covered and multiple layers of sorbed water form [39]. Similar trends have been reported for integral enthalpy of rice [30], maize, rough rice

and wheat [42], rice [10] and for starch powders [39]. The Figure 5 shows the effect of salt concentration on spreading pressure from this graph we can reveal that integral enthalpy increased with increasing salt concentration up to 3.5% salt but in case of 4% salt treated sample integral enthalpy low as compared to 3.5% salt.

Net integral entropy of preconditioned brown rice was calculated by applying Equation (10). Net integral entropy increased with increasing moisture content shown in Figure 6. The net integral entropy negative in magnitude being low at low moisture content while increasing moisture content integral entropy moves towards 0 kJ/mol K. The initial highly negative value of integral entropy at low moisture content was due to the first few percent of water is very tightly

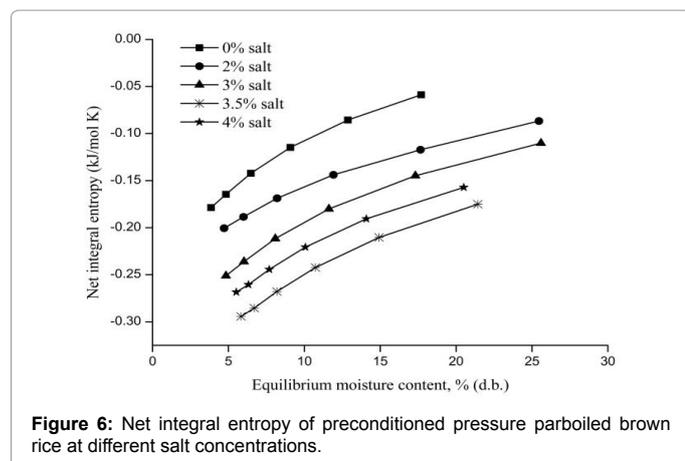


Figure 6: Net integral entropy of preconditioned pressure parboiled brown rice at different salt concentrations.

bound [39]. Similar trends were observed for integral entropy of starch powders [39], rice [10], potato [9] and cow pea [43]. Integral entropy decreased with increasing salt concentration (Figure 6) but in 4% salt treated sample net integral entropy high as compared to 3.5% salt treated sample.

Conclusions

On the basis of this work the following conclusion can be drawn. A non-linear regression analysis was used to evaluate the constants of the sorption models. The moisture sorption isotherm of preconditioned pressure parboiled brown rice at different salt concentrations adequately described by the MGAB equation. Net isosteric heat of sorption, calculated using the Clausis-Clapeyron equation. The model suggested by Kechau and Maalej gave the best relationship between net isosteric heat of sorption and equilibrium moisture content. Net isosteric heat of sorption decreased with increasing moisture content and increases with increasing salt concentration. Differential entropy of sorption can be characterised by an exponential model. Differential entropy decreased with increasing moisture content and increase with increasing salt concentration. Spreading pressure increased with increasing water activity and decrease with temperature. Net integral enthalpy decreased with increasing moisture content and increases with increasing salt concentration. Net integral entropy increased with increasing moisture content and decrease with increasing salt concentration.

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