Thermodynamics of sorption isotherms and storage stability of spray dried sweetened yoghurt powder

Dibyakanta Seth¹ · Kshirod Kumar Dash¹ · Hari Niwas Mishra² · Sankar Chandra Deka¹

Revised: 3 June 2018 / Accepted: 9 July 2018 / Published online: 25 July 2018
© Association of Food Scientists & Technologists (India) 2018

Abstract Sorption isotherm is a quantitative approach to predict the shelf life of dried foods. Adsorption isotherms of spray dried sweetened yoghurt powder (SYP) were determined by static gravimetric technique at 20, 30, 40 and 50 °C. The data obtained were fitted to eight different sorption models. A non-linear least square regression analysis was adopted to evaluate the model constants. The experimental sorption data were best fitted to four parameter Peleg model. The monolayer moisture contents found from GAB model were 4.88, 4.54, 3.86 and 3.52% at 20, 30, 40 and 50 °C, respectively. The maximum net isosteric heat of sorption and sorption entropy of SYP were 9.399 kJ/mol and 20.28 J/mol K, respectively. The Gibb's free energy change for sorption was in the range 3436.19–303.91 J/mol. The storage stability in terms of moisture content, thiobarbituric acid, free fatty acid, hydroxymethyl furfural values and starter counts of SYP packed in aluminium laminated polyethylene (ALPE) and low density polyethylene (LDPE) were studied along with their change kinetics. The relationship between the water vapour permeability of packaging materials and adsorbed moisture (determined from GAB equation) in powder was

used to predict the shelf life and was predicted as 28 and 44.44 days in LDPE and ALPE pouches, respectively.

Keywords Moisture adsorption isotherm · Sweetened yoghurt powder · Thermodynamic properties · Sorption model · Storage stability

List of symbols

a_w	Water activity
EMC	Equilibrium moisture content (kg/kg dry matter)
SSE	Sum of square error
SST	Total sum of square
RMSE	Root mean square error
χ^2	Reduced Chi square
R^2_{adj}	Adjusted correlation coefficient
T	Temperature (K)
$Q_{st,n}$	Net isosteric heat of sorption (kJ/mol)
Q_{st}	Isosteric heat of sorption(kJ/mol)
ΔH_{vap}	Latent heat of vaporization (kJ/mol K)
R	Universal Gas constant (8.314 J/mol K)
ΔS	Sorption entropy (J/mol K)
ΔG	Gibb's free energy change (J/mol)
M_o	Monolayer moisture content (kg/kg dry matter)
GAB	Guggenheim–Anderson–de Boer
BET	Brunauer–Emmett–Teller
db	Dry basis

Introduction

The short shelf life of *misti dahi* or sweetened yoghurt is attributable to its high moisture content. Recently, attempts have been made to investigate the potential use of spray drying as an alternative to conventional drying techniques

✉ Dibyakanta Seth
dibya05@tezu.ernet.in

Kshirod Kumar Dash
kshirod@tezu.ernet.in

Sankar Chandra Deka
sankar@tezu.ernet.in

¹ Department of Food Engineering and Technology, Tezpur University, Napaam, Tezpur, Assam 784028, India

² Department of Agricultural and Food Engineering, Indian Institute of Technology, Kharagpur, WB 721302, India

to dry yoghurt and yoghurt like products (Koc et al. 2010b). However, process technology for drying of sugar-rich yoghurt has not been developed so far though drying of sugar-rich and acidic foods has been studied extensively in the past. The stickiness issue in drying of sugar-rich foods has been resolved by the use of higher molecular weight substances (Adhikari et al. 2005; Bhandari et al. 1997; Goula et al. 2008).

While dealing with the dried food powders it becomes inevitable to control the water activity in a manner that results in better shelf life. In this context, the study on sorption isotherm of SYP is of paramount necessity for better prediction of shelf life. The relationship between the equilibrium moisture content (EMC) and water activity (a_w) of food over a range of values at a constant temperature is known as moisture sorption isotherm, which describes the binding potential of water to food materials. Isotherms provide valuable thermodynamic data of food materials which are useful for drying process design calculations and prediction of end point moisture content during a drying process (Langrish 2009). Theoretical prediction of shelf life of food materials is possible by the use of sorption isotherms (Koc et al. 2010a; Kumar and Mishra 2004). In addition to that, material properties like pore size distribution, porosity, surface area and crystallinity of food products can be found out, since the sorption behaviors are related to the structural features of food materials. Having got these information storage conditions and packaging systems can be designed for food materials (Basu et al. 2006; Chirife and Buera 1996).

Thermodynamic properties (enthalpy, entropy and Gibb's free energy) at the water binding sites are vital for predicting the energy requirements in drying and concentration processes (Yogendrarajah et al. 2015). Moreover, the determination of such critical parameters of food materials provides a closer insight into the microstructures and describe the water-sorption surface interaction. The relationship between the moisture content, energy of sorption and temperature is established by thermodynamic properties. The thermodynamic state of water absorbed by a food material and the amount of energy required to achieve a specific moisture content in a drying process can be calculated with the knowledge of isosteric heat of sorption (Goula et al. 2008; Sormoli and Langrish 2015). The differential heat of evaporation or sorption is denoted as isosteric heat of sorption which is calculated by Clausius–Clapeyron equation with the help of sorption isotherm model constants (Basu et al. 2006). The sorption entropy gives the status of the available sorption sites for water binding on the surface and the Gibb's free energy shows the spontaneity of the process (Yogendrarajah et al. 2015). Since, the moisture sorption isotherms of food materials are affected by the integrated hygroscopic properties of

different constituents in foods, the energy associated with the binding sites of sugar-rich foods such as SYP differs from the plain yoghurt powder.

Improper storage conditions can lead to moisture absorption by the powder which has many detrimental effects such as enzymatic browning and stale flavour developed due to Maillard reaction (Tamime and Robinson 1999). Oxidation of food constituents such as lipids is influenced by many factors such as heat treatment, storage temperature, moisture content, water activity and packaging materials (Stapelfeldt et al. 1997). Lipid oxidation of food changes its organoleptic properties. Because of lipid oxidation, some constituents like peroxide, thiobarbituric acid (TBA) increases during storage. Therefore, TBA is treated as a good indicator of oxidation in food. The extent of non-enzymatic browning in foods has been judged by the hydroxymethyl furfural (HMF) values (Kumar and Mishra 2004). The viability of starter bacteria also decreases during storage in yoghurt powder (Rybka and Kailasapathy 1997).

The objectives of this study were to measure the thermodynamic properties of moisture sorption of SYP and to predict the shelf life. Furthermore, the storage stability of SYP in terms of TBA, FFA and HMF contents (packed in LDPE and ALPE pouches) was investigated.

Materials and methods

Spray drying of sweetened yoghurt

Standardized (3% fat, 15% solid not fat) cow milk was taken and sweetened yoghurt was prepared by addition of 10% sugar, inoculated with NCDC-263 (mixed culture of *Streptococcus thermophilus* and *Lactobacillus delbrueckii* subsp. *bulgaricus*) and incubated at 42 ± 1 °C. A drying aid maltodextrin was mixed with sweetened yoghurt before drying. A laboratory scale spray dryer (Advanced Drying systems Pvt. Ltd., Mumbai) was used to dry sweetened yoghurt at 148 °C inlet air temperature, 0.54 L/h feed rate and 898 kPa atomization pressure (Seth et al. 2017). The powders were packed in aluminium laminated polyethylene pouches and stored in a desiccator before use for sorption study.

Determination of sorption isotherm

The static gravimetric technique was adopted to determine the equilibrium moisture content of SYP at eight different relative humidity selected between 7 and 85% and maintained by saturated salt solutions of NaOH, LiCl, MgCl₂, K₂CO₃, Mg(NO₃)₂, KI, NaCl and KCl (Iglesias and Chirife 1982). Air tight glass jars were filled with saturated

salt solutions into which beakers containing weight inside were placed and ensured that the neck of the beakers are above the solution levels. Beakers were firmly placed in the solution bath and samples (2 g each) were kept in small containers inserted to the individual beaker. Then the jars were tightened with lids and placed in experimental temperatures (20, 30, 40 and 50 °C). The equilibrium condition was ascertained when three consecutive measurements of weights showed a difference less than 0.001 g. This saturation condition was reached approximately after 20 days of storage. Triplicate samples were measured and used for data analysis. A petri plate was placed in a separate jar with RH higher than 75% to check and control the possible mould growth (Labuza 1984).

Modelling of sorption isotherms

The plots of equilibrium moisture content of SYP and the corresponding water activity at selected storage temperatures were used to generate sorption isotherms. In the present study, eight sorption models were used which have been proposed for sugar-rich dehydrated food powders in the literature (Iglesias and Chirife 1982; Koc et al. 2010a; Mundada and Hathan 2012; Sormoli and Langrish 2015; Varghese et al. 2009). A non-linear least-square regression analysis was done to evaluate the models. The curve fitting and regression analysis were performed using Origin-Pro 9.1 software. The goodness of fit for the models was evaluated with the sum of square error due to fit (*SSE*), the per cent root mean square error (*RMSE*), reduced Chi square (χ^2) and adjusted correlation coefficient (R^2) values. The equation giving the smallest χ^2 , *SSE*, *RMSE* and highest adjusted R^2 values was considered as best fitted. The measures of error in terms of *SSE*, *RMSE*, χ^2 and R^2 are calculated using the Eqs. 1–5 (Sormoli and Langrish 2015).

$$SSE = \sum_{i=1}^n w_i (M_i - \widehat{M}_i)^2 \quad (1)$$

$$SST = \sum_{i=1}^n w_i (M_i - \overline{M}_i)^2 \quad (2)$$

$$RMSE = \sqrt{\frac{SSE}{n - m}} \quad (3)$$

$$\chi^2 = \sum_{i=1}^n \frac{(M_i - \overline{M}_i)^2}{\sigma_i^2} \quad (4)$$

$$R_{adj}^2 = 1 - \frac{SSE(n - 1)}{SST(n - m)} \quad (5)$$

where M_i is the experimental EMC, $\widehat{M}_i$ is the predicted EMC from the fitting curve, w_i is the weightage applied to

each data point and was set to unity in this analysis. *SST* is the total sum of square value, n is the number of experimental data point and m is the number of coefficients in each equation.

The standardized residuals (difference of measured and predicted moisture content) were calculated (Eq. 1) and plotted as functions of water activity. The residual plots ascertained definite pattern or randomness. A model is considered acceptable when the residual points were centered on the origin in horizontal plane.

Thermodynamic properties of sorption phenomena

Net isosteric heat of sorption is defined as the total heat of sorption of water in food in excess of the heat of vaporization of pure water at a constant moisture content, which can be found out from Clausius–Clapeyron equation (Eq. 6).

$$\left[\frac{d(\ln a_w)}{d\left(\frac{1}{T}\right)} \right]_M = \frac{-Q_{st,n}}{R} \quad (6)$$

and

$$Q_{st,n} = Q_{st} - \Delta H_{vap} \quad (7)$$

where a_w is the water activity, T is temperature (K), $Q_{st,n}$ is net isosteric heat of sorption (kJ/mol water), Q_{st} is the isosteric heat of sorption, ΔH_{vap} is heat of vaporization of water in pure form (kJ/mol water), R is the universal gas constant (8.314 J/mol K).

The graph of the natural logarithm of the water activity was plotted against the inverse of absolute temperature. The net isosteric heat of sorption was calculated from the slope of the regression line. The sorption entropy (ΔS) is related to the net isosteric heat of sorption which denotes the energy associated on the sorption sites can be derived from Eq. (7) and is presented in Eq. (8).

$$-\ln a_w = \frac{Q_{st,n}}{RT} - \frac{\Delta S}{R} \quad (8)$$

The predicted GAB model coefficients were used to determine the sorption entropy at specific moisture content. It was calculated from the intercept ($\Delta S/R$) of the fitted curve of $\ln(a_w)$ versus $1/T$. Gibb's free energy indicates the sorbent's affinity for water and refers to the whether or not the sorption is a spontaneous process (Yogendrarajah et al. 2015). It was calculated for SYP using Eq. (9).

$$\Delta G = -RT \ln a_w \quad (9)$$

Water activity data generated from GAB model at specific equilibrium moisture content was used to calculate Gibb's free energy change at different absolute temperatures.

Determination of shelf life

The HDPE and ALPE pouches (138 mm × 96 mm) filled with 20 g SYP samples were heat sealed to ensure leak proof and minimum headspace was maintained inside the pouches. A desiccator kept at $38 \pm 1^\circ\text{C}$ was maintained an environment of 90% relative humidity using a saturated solution of potassium nitrate and was used to store eight sample pouches. It was ensured that all the pouches were exposed to the same environmental condition. Moisture content was analyzed gravimetrically at 7 day interval up to 49 days. The shelf life was calculated using the following equation.

$$\int d\theta = \frac{W_s}{P^*KA} \int_{X_i}^{X_c} \frac{dX}{RH - a_w} \quad (10)$$

where θ = shelf-life (days), W_s = weight of dry solids (g), P^* = saturated vapour pressure of water at ambient temperature (Pa), K = water vapour permeability of the packaging material ($\text{kg m}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$), A = area of the package (m^2), RH = relative humidity of the environment in which the package is placed (%), a_w = water activity of the powder, X_i = initial moisture content (% db) and X_c = critical moisture content (% db).

The water vapour permeability, K ($\text{kg m}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$) of the packaging materials was calculated as given in Eq. (11) (Labuza 1984).

$$K = \frac{dw/d\theta_p}{A_p P^*} \quad (11)$$

where $dw/d\theta_p$ = slope of the straight line of the graph plotted between the time θ_p and weight of silica gel kept within the packaging material, A_p = surface area of the packaging material (m^2), and P^* = saturation vapour pressure of water at the packaging environment temperature $38 \pm 1^\circ\text{C}$ (Pa).

Assessment of quality changes in SYP

Quality parameters of SYP were analyzed taking one pouch at a time from desiccator at 7 day intervals. Moisture content was determined by oven drying method. TBA value (OD at 532 nm) was measured according to the method of King (1962) and Kumar and Mishra (2004). The FFA content was measured using the method described by Deeth (2006). The HMF content was determined according to the method suggested by Keeney and Bassette (1959). Serial dilution method was used to enumerate the bacterial counts. *S. thermophilus* was enumerated by growing them in M17 agar media (HiMedia) and incubated at 37°C for 48 h whereas MRS agar (HiMedia) was used for *L.*

delbrueckii subsp. *bulgaricus* enumeration which was incubated at 37°C for 72 h. Majority of research on food products reported either zeroth or first order degradation of quality parameters. So, these two kinetics models were chosen for describing the rate of reactions. Zeroth order reaction:

$$C = C_o \pm k_o t \quad (12)$$

First order reaction:

$$\ln C = \ln C_o \pm k_1 t \quad (13)$$

Statistical analysis

Analysis of variance was carried out to analyse the chemical and microbiological properties of stored SYP using SPSS software (SPSS 2002). The factors included in the analysis were packaging material and storage time.

Results and discussion

Fitting of sorption isotherm models to experimental data

The adsorption isotherms of SYP at 20, 30, 40 and 50°C are shown in Fig. 1. The isotherms are sigmoidal in nature, the behavior is typical for yoghurt powders (Koc et al. 2010a; Kumar and Mishra 2006) and other dairy products (Varghese et al. 2014). The adsorption isotherms of SYP showed type III behaviour of BET classification (Labuza 1984). Dissolution of solutes like sugars in water is explained as the basis of type III isotherm formation (Rao and Rizvi 1994). An increase in temperature concomitantly increased a_w at constant moisture content and if a_w kept

Fig. 1 Moisture sorption isotherms of sweetened yoghurt powder at 20, 30, 40 and 50°C showing the fitted curves of GAB model. *The data are presented in triplicate

constant the increase in temperature decreased the adsorbed moisture. This indicates that the SYP becomes less hygroscopic at higher temperatures. This phenomenon could be explained by the water binding potential of yoghurt components such as proteins and carbohydrates. At low temperature the water binding potential is more compared to that at high temperature and thus it was evident that SYP exhibited less hygroscopicity at higher temperatures. It is also reported that at higher temperature, the kinetic energy of the water molecules is high and the water absorption is low at a given a_w (Demertzis et al. 1989). Palipane and Driscoll (1992) explained this phenomenon as the breaking away of water molecules from the sorption sites when activated at higher energy levels and decreases the *EMC*. Similar findings have been reported in literature of sorption isotherm study of yoghurt powders (Koc et al.

2010a; Varghese et al. 2009). A sharp increase in *EMC* was observed at higher a_w ($a_w > 0.50$) for all the temperatures studied and could be explained by the dissolution of sugar in the sorbed water vapour (Kaymak-Ertekin and Gedik 2004; Maroulis et al. 1988). The sugar percent in the dried sweetened yoghurt was about 45%, therefore comparison of sorption isotherms of SYP with that of sugar-rich food powders is quite justifiable.

The suitability of eight selected equations to model the dependence of *EMC* of SYP on a_w in temperature range 20–50 °C was investigated and the comparison is given in Table 1. The models with minimum *SSE*, χ^2 and maximum adjusted R^2 were considered best fitted. In the present study a model with adjusted correlation coefficient, $R^2_{adj} > 0.99$ was regarded as best fit. It can be observed from the statistical model indices that Peleg equation could model

Table 1 Estimated parameters of fitted models to the experimental data for the sorption isotherm of spray-dried sweetened yoghurt powder at 20, 30, 40 and 50 °C

Model	Temperature	Goodness of fit parameters				Model coefficients			
		<i>SSE</i>	% <i>RMSE</i>	χ^2	R^2_{adj}	A	B	C	D
GAB	20	0.00151	0.00848	7.18×10^{-5}	0.9932	0.04881, M_o	10.5776, C	1.0079, K	–
	30	0.00168	0.00896	8.03×10^{-5}	0.9906	0.04546, M_o	10.8598, C	1.0018, K	–
	40	0.00115	0.00741	5.48×10^{-5}	0.9921	0.03863, M_o	17.6687, C	1.0128, K	–
	50	0.00116	0.00742	5.51×10^{-5}	0.9915	0.0352, M_o	20.1736, C	1.0218, K	–
BET	20	0.00159	0.00849	7.21×10^{-5}	0.9932	0.05103, M_o	8.35015, C	–	–
	30	0.00169	0.00876	7.68×10^{-5}	0.9910	0.04592, M_o	10.29551, C	–	–
	40	0.00133	0.00777	6.03×10^{-5}	0.9913	0.04134, M_o	12.00189, C	–	–
	50	0.00165	0.00865	7.48×10^{-5}	0.9885	0.03971, M_o	9.75673, C	–	–
Modified Smith	20	0.01313	0.02443	5.97×10^{-4}	0.9435	– 9.50571	0.475	– 9.41984	0.47901
	30	0.01012	0.02145	4.60×10^{-4}	0.946	– 14.49752	0.48314	– 14.43236	0.48588
	40	0.0102	0.02153	4.63×10^{-4}	0.9332	– 19.4955	0.48734	– 19.44128	0.48926
	50	0.01125	0.02262	5.11×10^{-4}	0.9212	– 24.49492	0.48983	– 24.44523	0.49139
Modified Halsey	20	0.0009	0.00663	4.39×10^{-5}	0.9858	0.62989	– 0.18146	1.08118	–
	30	0.0012	0.0074	5.47×10^{-5}	0.9836	0.648	– 0.1263	1.10549	–
	40	0.001	0.00674	4.54×10^{-5}	0.9834	0.65611	– 0.0972	1.093	–
	50	0.00115	0.00723	5.22×10^{-5}	0.9819	0.66026	– 0.0777	1.05857	–
Modified Oswin	20	0.00259	0.01085	1.18×10^{-4}	0.9888	– 9.50746	0.47979	0.76034	–
	30	0.00248	0.01063	1.13×10^{-4}	0.9867	– 14.53607	0.48727	0.74152	–
	40	0.00269	0.01106	1.22×10^{-4}	0.9824	– 19.56594	0.491	0.75308	–
	50	0.00291	0.0115	1.32×10^{-4}	0.9796	– 24.33831	0.48811	0.77401	–
Modified Henderson	20	0.00655	0.01726	2.98×10^{-4}	0.9718	– 0.60398	– 27.28229	0.74633	–
	30	0.00562	0.01598	2.55×10^{-4}	0.9700	0.73751	– 23.37736	0.7674	–
	40	0.00597	0.01648	2.71×10^{-4}	0.9609	– 0.59492	– 48.63454	0.75031	–
	50	0.00608	0.01662	2.76×10^{-4}	0.9574	– 0.96188	– 55.2147	0.71446	–
Peleg	20	7.47×10^{-4}	0.00611	3.74×10^{-5}	0.9965	0.60873, k_1	0.08893, k_2	5.45555, n_1	0.42623, n_2
	30	5.45×10^{-4}	0.00522	2.73×10^{-5}	0.9968	0.07727, k_1	0.52962, k_2	0.38677, n_1	5.19405, n_2
	40	2.78×10^{-4}	0.00373	1.39×10^{-5}	0.9980	0.52035, k_1	0.0713, k_2	5.64975, n_1	0.36232, n_2
	50	3.16×10^{-4}	0.00398	1.58×10^{-5}	0.9976	0.53323, k_1	0.06626, k_2	5.92688, n_1	0.35242, n_2
Iglesias and Chirife	20	0.0012	0.0074	5.47×10^{-5}	0.9948	0.02898	0.05482	–	–
	30	0.00157	0.00845	7.14×10^{-5}	0.9916	0.02807	0.04915	–	–
	40	0.00084	0.00617	8.38×10^{-5}	0.9945	0.02565	0.04441	–	–
	50	0.00079	0.00601	7.95×10^{-5}	0.9944	0.02265	0.04297	–	–

adsorption behavior of SYP better ($R_{adj}^2 > 0.996$ and smallest χ^2 value of 3.74×10^{-5}). A randomness in the standardized residual plots was observed in all the models and considered as good fit. Mere fitting of experimental data to a sorption model cannot guarantee its validation, rather a mechanistic approach is needed for a full proof validation (Chirife et al. 1992). The GAB model which is semi-empirical in nature has some parameters of biological importance compared to the complete empirical Peleg model. Though the Peleg model fitted well to the experimental data, the parameters of GAB model were taken for thermodynamic analysis of SYP.

The information on monolayer moisture (M_o) of food products is vital for the storage stability. It is a critical parameter which ensures that no associated reaction takes place if moisture content of foods remain below M_o , because it indicates a strong binding potency of water on the surface (Al-Muhtaseb et al. 2002). The GAB model estimated M_o 's of 4.88, 4.54, 3.86 and 3.52% at 20, 30, 40 and 50 °C, respectively and the corresponding M_o 's estimated by BET model were 5.10, 4.59, 4.13 and 3.94%. The results evinced that the M_o 's decreased with increasing temperature which could be explained by the higher activation energy theory. In comparison to yoghurt powder, SYP had higher M_o values, and may be explained by the presence of hygroscopic components such as sucrose in SYP (Koc et al. 2010a; Kumar and Mishra 2006). The binding potency of water in terms of heat of sorption of monolayer moisture (GAB parameter C) was higher than that of multilayer moisture (GAB parameter K) (Table 1).

Thermodynamic properties

The net isosteric heat of sorption (Eq. 6) exhibited strong dependency on *EMC* of SYP (Fig. 2). The net isosteric heat was maximum (9.399 kJ/mol) at the lowest EMC (5% db) which decreased exponentially with the increase in EMC. This finding is also corroborated by several workers (Sormoli and Langrish 2015; Yogendrarajah et al. 2015). This could be attributed to the availability of highly active polar sites initially that require greater energy of interaction. Once the available polar sites become less the energy of binding also diminishes (Arslan and Toğrul 2005). The isosteric heat of sorption decreased swiftly up to 10% moisture content (db) followed by gradual decrease with increasing moisture content. This implied that the water bound in the 'monolayer region' is difficult to remove compared to the 'condensed water region' of isotherm. The heat of sorption of SYP approached the latent heat of vaporization of pure water above 35% moisture content (db) ($Q_{st,n} < 1.0$ kJ/mol).

Like isosteric heat of sorption, sorption entropy exhibited strong dependency on *EMC* (Fig. 2). The sorption

Fig. 2 Effect of moisture content on net isosteric heat of sorption and sorption entropy of sweetened yoghurt powder

entropy value of SYP was in the range of 20.28–0.93 J/mol K for the studied EMC range of 5–40% (db). At higher moisture content, there are more water molecules on the surface and making active binding sites less available and thus less chance of sorption which results in decreased entropy. Contrary to this, the available active binding sites are more at lower moisture content and resulted in increased entropy (Yogendrarajah et al. 2015). In the present study, the sorption sites could have been influenced by the more hygroscopic components in SYP.

The variation in Gibb's free energy change (ΔG) with respect to *EMC* at four temperature levels during adsorption is illustrated in Fig. 3. The graph clearly indicates that the ΔG decreased exponentially with EMC. The ΔG values for SYP varied from 3436.19 to 303.91 J/mol at varied moisture content. In general hydrophilic food materials exhibit higher ΔG values because they show greater affinity to water sorption (Yogendrarajah et al. 2015). The

Fig. 3 Gibb's free energy change during sorption of moisture in sweetened yoghurt powder at 20, 30, 40 and 50 °C

results showed that the ΔG value was higher at minimum storage temperature at a specific moisture content and could be explained by energy which is required to make the sorption sites available is more at low temperature. Further, it was elucidated that the rate of change of ΔG was less at higher moisture contents and the change was pronounced at moisture content in short of monolayer moisture content (M_o) and results are in line with the findings of Taitano et al. (2012).

Shelf life prediction and storage studies

The shelf life of SYP packed in LDPE and ALPE and stored at $38 \pm 1^\circ\text{C}$ was determined using Eq. 10. The water vapour permeability of LDPE and ALPE was calculated using Eq. 11 and was found to be 3.46×10^{-7} and $1.48 \times 10^{-8} \text{ kg m}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$, respectively. The initial moisture content (X_i) of SYP was 4.85% (db). The results showed that the moisture content of powder gradually increased with storage time and the moisture gain was pronounced in SYP packed in LDPE pouch (Fig. 4a). The final moisture contents of SYP packed in LDPE and ALPE pouches after 49 days storage were 8.92 and 7.96% (db), respectively. The final moisture content decided was based on the free flowness of powder and was in the range of 7.27–8.26% (db) and was considered as the critical moisture content (X_c). At storage temperature of 38°C , the GAB parameters, M_o , C , and K were 4.06%, 15.27 and

1.0094, respectively. These values were used to calculate the corresponding water activity. The area of the pouch was 0.01325 m^2 ($13.8 \text{ cm} \times 9.6 \text{ cm} \times 2$). The total solid (W_s) in 20 g sample was 0.019 kg and the saturated vapour pressure at ambient temperature was 3169 Pa. Applying all these values in Eq. 10, the shelf life of SYP was calculated as 28 and 44.44 days in LDPE and ALPE pouches, respectively. Furthermore, reconstitution of SYP was done with distilled water. A total solid content of 40% in reconstituted yoghurt was acceptable rheologically and sensorially (Seth et al. 2018). The reconstituted sweetened yoghurt could be kept up to 8 days in refrigerated condition without any quality deterioration of any quality.

Kinetics of quality changes in SYP during storage

Initially, the FFA of SYP was 75.3μ equivalent/g and at the end of 49 days of storage the value was 108.02 and 102.59μ equivalent/g for LDPE and ALPE pouches respectively (Fig. 4c). In the present study, both the storage period and packaging material exhibited significant effect on FFA ($P < 0.01$). FFA is liberated as a result of saponification or cleaving of fats during hydrolysis (Belitz et al. 2009). Kinetics study confirmed zeroth order reaction in FFA formation irrespective of any packaging material ($R^2 > 0.97$) (Table 2). The FFA formation is reported to have detrimental effects on the curd strength and starter growth (Seth and Das 2011).

Fig. 4 Changes in chemical quality parameters and starter count during accelerated storage of sweetened yoghurt powder stored in ALPE and LDPE

Table 2 Zeroth and First order kinetics of chemical quality changes and starter count reduction of sweetened yoghurt powder stored in LDPE and ALPE during storage

Packaging material	LDPE						ALPE					
	Zero order			First order			Zero order			First order		
	K_0	C_0	R^2	K_1	C_0	R^2	K_0	C_0	R^2	K_1	C_0	R^2
MC	0.6239	4.3724	0.9873	1.8371	4.6307	0.8602	0.5425	4.2071	0.9831	1.5911	4.4394	0.8499
HMF	8.6382	574.94	0.9891	29.134	575.19	0.9278	7.1475	573.77	0.9803	23.619	574.63	0.8827
FFA	4.8289	67.834	0.9816	15.538	68.968	0.8381	3.952	68.829	0.9734	12.588	69.927	0.8144
TBA	0.0316	0.0775	0.9849	0.1078	0.0768	0.9442	0.0299	0.0608	0.9859	0.0974	0.0661	0.8648
<i>S. thermophilus</i>	– 9.2927	69.072	0.9686	– 32.47	70.291	0.9749	– 8.0754	67.964	0.9645	– 28.33	69.179	0.9789
<i>L. bulgaricus</i>	– 8.1022	59.116	0.9599	– 28.54	60.495	0.9825	– 8.0091	60.237	0.9697	– 27.96	61.264	0.9748

Thiobarbituric acid (TBA) as a measure of lipid peroxidation in biological systems is a preferred method of quality check (Stapelfeldt et al. 1997). The TBA in terms of OD values of SYP stored in LDPE and ALPE were increased to 0.322 and 0.294, respectively from initial OD value of 0.104 (Fig. 4b). The effects of both storage time and packaging materials on TBA value was significant ($P < 0.01$) and fitted to zeroth order equation ($R^2 > 0.98$) (Table 2).

The hydroxymethyl furfural (HMF), which is an intermediate product of Maillard reaction, provides the information of the extent of browning of food products. Initially, the HMF of SYP was 580.63 $\mu\text{mol/kg}$ and increased to 645.97 and 635.61 $\mu\text{mol/kg}$ in LDPE and ALPE pouches, respectively at the end of 49 days and followed zeroth order kinetics. Results illustrated that the HMF content was significantly affected by storage period and packaging material ($P < 0.001$). Since, HMF is synthesized from glucose, the extent of its formation depends on the lactose present in milk products (Mistry and Pulgar 1996).

In the beginning, the *S. thermophilus* and *L. bulgaricus* counts of SYP were 65.33×10^6 and 57.67×10^6 cfu/ml, respectively. The *S. thermophilus* count decreased to 1.33 and 6.67×10^6 for SYP stored in LDPE and ALPE pouches, respectively whereas, the corresponding decrease was 2.5×10^5 and 1.36×10^6 cfu/ml for *L. bulgaricus*. The reduction in the *S. thermophilus* counts was significantly affected by storage time ($P < 0.001$) rather than the packaging material ($P < 0.05$). Similar trend was observed for *L. bulgaricus* and several authors have also reported similar observations (Kumar and Mishra 2004)

Conclusion

Eight sorption models proposed in this work were tested to determine the best fit for experimental data corresponding to moisture adsorption by sweetened yoghurt powder (SYP). Of those, Peleg equation was found to be the best. The adsorption isotherm of SYP followed type III classification and the product showed less hygroscopicity at higher temperature storage. The net isosteric heat of sorption and sorption entropy were highest below the monolayer moisture content and it decreased with increasing moisture content. The Gibb's free energy change decreased exponentially with increasing moisture content. The relationship between the thermodynamic properties and EMC could be a useful tool for shelf life prediction of SYP. The shelf life of SYP predicted at accelerated storage condition (38 ± 1 °C, 90% RH) was 28 and 44.44 days in LDPE and ALPE pouches, respectively. Quality deterioration in SYP (increase in moisture

content, FFA, TBA and HMF values) was observed with storage period. Results of the present investigation have the credentials to support that the changes of all these quality parameters followed zeroth order reaction except the starter count which followed first order kinetics and the change of SYP quality parameters was faster in LDPE than in ALPE packaging material.

Acknowledgements The first author would like to acknowledge the support received from the Ministry of Food Processing Industries (MoFPI) (11/MFPI/R&D/11), New Delhi, India for their financial support.

Compliance with ethical standards

Conflict of interest All the authors declare that they have no conflict of interest.

References

- Adhikari B, Howes T, Lecomte D, Bhandari BR (2005) A glass transition temperature approach for the prediction of the surface stickiness of a drying droplet during spray drying. *Powder Technol* 149:168–179
- Al-Muhtaseb AH, McMinn WAM, Magee TRA (2002) Moisture sorption isotherm characteristics of food products: a review. *Food Bioprod Process* 80:118–128
- Arslan N, Toğrul H (2005) Moisture Sorption Isotherms for Crushed Chillies. *Biosys Eng* 90:47–61
- Basu S, Shivhare US, Mujumdar AS (2006) Models for sorption isotherms for foods: a review. *Dry Technol* 24:917–930
- Belitz HD, Grosch W, Schieberle P (2009) *Food chemistry*, 4th edn. Springer, Berlin
- Bhandari BR, Datta N, Crooks R, Howes T, Rigby S (1997) A semi-empirical approach to optimise the quantity of drying aids required to spray dry sugar-rich foods. *Dry Technol* 15:2509–2525
- Chirife J, Buera MD (1996) Water activity, water glass dynamics, and the control of microbiological growth in foods. *Crit Rev Food Sci* 36:465–513
- Chirife J, Timmermann EO, Iglesias HA, Boquet R (1992) Some features of the parameter-K of the Gab equation as applied to sorption isotherms of selected food materials. *J Food Eng* 15:75–82
- Deeth HC (2006) Lipoprotein lipase and lipolysis in milk. *Int Dairy J* 16:555–562
- Demertzis PG, Riganakos KA, Kontominas MG (1989) Water sorption isotherms of crystalline raffinose by inverse gas-chromatography. *Int J Food Sci Tech* 24:629–636
- Goula AM, Karapantsios TD, Achilias DS, Adamopoulos KG (2008) Water sorption isotherms and glass transition temperature of spray dried tomato pulp. *J Food Eng* 85:73–83
- Iglesias HA, Chirife J (1982) *Handbook of food isotherms: water sorption parameters for food and food components*. Academic Press, New York
- Kaymak-Ertekin F, Gedik A (2004) Sorption isotherms and isosteric heat of sorption for grapes, apricots, apples and potatoes. *Lebensm-Wiss Technol* 37:429–438
- Keeney M, Bassette R (1959) Detection of intermediate compound in early stages of browning reaction in milk products. *J Dairy Sci* 42:945–960
- King RL (1962) Oxidation of milk fat globule membrane material. I. Thiobarbituric acid reaction as a measure of oxidized flavour in milk and model system. *J Dairy Sci* 45:1165–1171
- Koc B, Yilmazer MS, Balkir P, Ertekin FK (2010a) Moisture sorption isotherms and storage stability of spray-dried yogurt powder. *Dry Technol* 28:816–822
- Koc B, Yilmazer MS, Balkir P, Ertekin FK (2010b) Spray drying of yogurt: optimization of process conditions for improving viability and other quality attributes. *Dry Technol* 28:495–507
- Kumar P, Mishra HN (2004) Storage stability of mango soy fortified yoghurt powder in two different packaging materials: HDPP and ALP. *J Food Eng* 65:569–576
- Kumar P, Mishra HN (2006) Moisture sorption characteristics of mango-soy-fortified yogurt powder. *Int J Dairy Technol* 59:22–28
- Labuza TP (1984) Typical sorption isotherms. In: Bell L, Labuza T (eds) *Moisture Sorption American Association of Cereal Chemists*, St. Paul, Minnesota, pp 1–4–8–21
- Langrish TAG (2009) Multi-scale mathematical modelling of spray dryers. *J Food Eng* 93:218–228
- Maroulis ZB, Tsami E, Marinoukouris D (1988) Application of the GAB model to the moisture sorption isotherms of dried fruits. *J Food Eng* 7:63–78
- Mistry VV, Pulgar JB (1996) Physical and storage properties of high milk protein powder. *Int Dairy J* 6:195–203
- Mundada M, Hathan BS (2012) Studies on moisture sorption isotherms for osmotically pretreated and air-dried pomegranate arils. *J Food Process Pres* 36:329–338
- Palipane KB, Driscoll RH (1992) Moisture sorption characteristics of in shell macadamia nuts. *J Food Eng* 18:63–76
- Rao MA, Rizvi SSH (1994) *Engineering properties of foods*, 2nd edn. Marcel Dekker Inc, New York
- Rybka S, Kailasapathy K (1997) Effect of freeze drying and storage on the microbiological and physical properties of AB-yoghurt. *Milchwissenschaft* 52:390–394
- Seth R, Das A (2011) *Quality of milk in relation to cheese making*. National Dairy Research Institute, Karnal
- Seth D, Mishra HN, Deka SC (2017) Effect of spray drying process conditions on bacteria survival and acetaldehyde retention in sweetened yoghurt powder: an optimization study. *J Food Process Eng* 40:e12487
- Seth D, Mishra HN, Deka SC (2018) Effect of hydrocolloids on the physico-chemical and rheological properties of reconstituted sweetened yoghurt powder. *J Sci Food Agric* 98:1696–1702
- Sormoli ME, Langrish TAG (2015) Moisture sorption isotherms and net isosteric heat of sorption for spray-dried pure orange juice powder. *Lebensm-Wiss Technol* 62:875–882
- SPSS (2002) *SPSS 11.5.0 for Windows software*, SPSS Inc, Chicago
- Stapelfeldt H, Nielsen BR, Skibsted LH (1997) Effect of heat treatment, water activity and storage temperature on the oxidative stability of whole milk powder. *Int Dairy J* 7:331–339
- Taitano LA, Singh RP, Lee JH, Kong F (2012) Thermodynamic analysis of moisture adsorption isotherms of raw and blanched almonds. *J Food Process Eng* 35:840–850
- Tamime AY, Robinson RK (1999) *Yoghurt: Science and Technology*, 2nd edn. CRC Press, Florida
- Varghese S, Ramachandran SV, Mishra HN (2009) Moisture sorption characteristics of curd (Indian yogurt) powder. *Int J Dairy Technol* 62:85–92
- Varghese KS, Radhakrishna K, Bawa AS (2014) Moisture sorption characteristics of freeze dried whey-grape beverage mix. *J Food Sci Tech Mys* 51:2734–2740
- Yogendrarajah P, Samapundo S, Devlieghere F, de Saeger S, de Meulenaer B (2015) Moisture sorption isotherms and thermodynamic properties of whole black peppercorns (*Piper nigrum L.*). *Lebensm-Wiss Technol* 64:177–188