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# Moisture sorption isotherm and isosteric heat of sorption characteristics of starch based edible films containing antimicrobial preservative

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**Abstract**: Moisture sorption isotherms (MSI) of antimicrobial (benzoic acid, potassium sorbate, and sodium propionate) incorporated cornstarch based self-supporting edible films have been determined at 25, 35, and 45$^{o}$C following isopiestic vapour transfer technique. Antimicrobials show positive treatment effect on the equilibrium moisture content. The MSI of these films are best described with modified Oswin model among the three models (GAB, modified Oswin and Peleg) attempted. MSI at 25°C but at 35 and 45°C deviates more from that of control (no antimicrobial) - showing lower water activity with benzoic acid incorporated films. While the binding sites on the film has been found to be heterogeneous, temperature shows direct effect on moisture sorption with potassium sorbate and sodium propionate. The net isosteric heat of sorption decreases exponentially as the film moisture content increases, and at lower moisture level it follows the order: potassium sorbate> sodium propionate> benzoic acid >control.

**Keywords: Moisture sorption, edible films, antimicrobial containing edible films**

## Introduction

Self-supporting edible films (SSEF), prepared with different combinations of food grade constituents like, carbohydrates, proteins and lipids, and hydrophilic plasticizers including polyhydric alcohols, water etc. have excellent oxygen and aroma barrier properties (Das and Bal, 1999); thus quality of aroma containing materials can be preserved well by packaging with these films. Moreover, water dispersible and edible character of these films facilitates packaging of specific food additives in separate pouches which can go along in the cooking medium, dispersing both additives and pouches together. This helps in addition of pre-measured quantity of additives for better quality control in food processing and reduces the use of alternative synthetic throwaway pouches (Ninomiya *et al*., 1992; Das and Bal, 1999; Yang *et al*., 2004; O'Riordan and O'Sullivan 2005; Patel and Thanawala, 2008). Due to hydrophilic character, the ingredients in the films have a tendency to adsorb/desorb moisture depending on environmental relative humidity during storage. As the interaction among the plasticized ingredients depends on the net plasticizer content (Changa *et al*., 2006), physical and mechanical properties of the film is dependent on its ultimate moisture content.

Water activity ($a_w$) is a measure of the energy status of the moisture content in a system, and controls several properties of biopolymer based materials; high water activity leads to chemical and microbial instability. The equilibrium relationship between $a_w$ (ranging within 0.0-1.0) and the corresponding moisture content at any particular temperature is represented by moisture sorption isotherm (MSI), which is most important in design of drying, packaging and storage systems. Representation of sorption data with best fit sorption model could be used as a tool for achieving these designs. MSI of edible films prepared with various raw materials like, corn starch, tapioca starch, cellulose derivatives, whey protein, peanut proteins, etc. has been modeled by several workers (Ayranci, 1996; Jangchud and Chinnan, 1999; Coupland *et al*., 2000; Bertuzzi *et al*., 2003).

The binding energy involved between sorbate (water) and sorbents, called the net isosteric heat of sorption ($q_{st}$), is dependent on moisture content of a material and is very important to ascertain its response to different storage temperature and

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relative humidity. Net isosteric heat of sorption can be estimated by Clausius – Clayperon equation (Al-Muhtaseb *et al*., 2004) using MSI data at different temperatures. Since SSEF is made from hydrophilic raw material it is worth estimating the $q_{st.}$ However, not much information is available on this aspect.

Inspite of the advantages as above, the edible films are susceptible to be infected with air-borne microbes, particularly at high relative humidity environment, thus makes them unfit to use. Incorporation of antimicrobial preservatives in the film, therefore, may be resorted to. Nadarajah (2005) and, Ozdemir and Floros (2001) have reported the efficacy of incorporated antimicrobials in SSEF by measuring their diffusion in the surrounding medium. One patent (Virgallito and Zang, 2006) is available on incorporation of fruit acid to chewable edible films to act as oral refresher. However, limited information is available on incorporation of antimicrobials in SSEF in influencing their MSIs.

The present work aims to study the effect of incorporation of three antimicrobials like, potassium sorbate (PS), sodium propionate (SP), and benzoic acid (BA) in the film formulation containing gelatinized cornstarch and plasticizers, on the MSI of the films at three temperatures. This is followed by modeling of the respective MSI. Additionally, the correlation between the net isosteric heat of sorption and moisture content of the each type of film has been attempted.

## Materials and Methods

*Materials*

Corn starch was procured from local market. Laboratory or analar grade chemicals like hydroxy propylmethyl cellulose, BA, SP, PS, polyethylene glycol (400) and glycerol (87%), and glass distilled water were used.

*Methods*

*Film preparation*

Corn starch (5.75 g), hydroxypropyl methyl cellulose (0.25 g), antimicrobial agent (0.16 g), and plasticizers like glycerol (1.46 ml), polyethylene glycol (1 ml) and water (78 ml) were taken in a 250 ml conical flask. The slurry was uniformly mixed with a spatula and heated in a boiling water bath for 10-12 min. The hot gelatinized blend was spread on a polypropylene plate with the help of Thin Layer Chromatography (TLC) applicator. The thickness of wet film was adjusted to 2 mm. The cast film was dried in an incubator at 40 °C for 24 h. The dried film was peeled off from the plate and stored in between two ordinary writing paper sheets for about three months to facilitate structural reorganization of interactive ingredients in the film matrix (Das, 2008).

*Determination of equilibrium moisture content (EMC)*

Equilibrium moisture contents were determined by isopiestic vapour transfer technique by exposing the films to constant relative humidity environment created by saturated solution of a particular salt (Labuza, 1984). Eight different salts viz., LiCl, $CH_3COOK$, $MgCl_2$, $K_2CO_3$, $MgNO_3$, $NaNO_3$, NaCl and KCl were used to maintain respective water activity ($a_w$) inside separate vacuum desiccators in the range of 0.1 to 0.9 and at three temperatures, viz., 25, 35 and 45°C. Water activity for each of the saturated salt solutions at these temperatures were estimated using equation described elsewhere (Labuza, 1984). Films were kept inside the desiccators for about three weeks for equilibration and final moisture content for each film was determined by oven drying method at 105°C for 24 hours. Each set of experiment was repeated thrice and average values and corresponding standard deviation were recorded. The effect of antimicrobial agent (treatment) on the respective mean value has been analyzed statistically following analysis of variance (F-test) at 1 or 5% levels of significance using single factor experiment with completely randomized design with equal replications (Gomez and Gomez, 1984). Significant F-test assures that the observed difference among the treatment means is real and not due to a chance. Further, the least significant differences (LSD) amongst the mean EMC value of different films at any particular $a_w$ and temperature were estimated at 1 or 5 % probability levels to ascertain any significant difference among the pair of treatments (Gomez and Gomez, 1984). All the statistical calculations were done using Microsoft Excel 2000 (Microsoft Corp., USA).

*Fitting of EMC data to various isotherm models*

Experimental data were fitted to three MSI models, such as Guggenheim-Anderson-De Boer (GAB), Peleg and modified Oswin models (Table 1), where $a_w$ represents the equilibrium relative humidity in decimal; M is the equilibrium moisture content in % (db); $M_0$ is the monolayer moisture content value in % (db); T is the temperature in °C; A, B, C, K, $K_1$, $K_2$, $n_1$, $n_2$ and x are sorption isotherm constants specific to each equation. Non-linear regression analysis was used to calculate the respective constants using software like, Microsoft excel 2000 (Microsoft Corp., USA), Systat 8.0 (SPSS, Inc., 1998), and Origin 6.0 (Microcal Software, Inc., 1998).

*Goodness of fit to the models*

To evaluate the goodness-of-fit for each of the models (Table 1), the co-efficient of determination ($r^2$), mean relative percentage deviation modulus (MRE %), the root mean square error (RMSE), and residual plots were used. The residual plot is a plot of ($M_i$ - $M_{pi}$) versus $M_i$. MRE and RMSE were calculated as follows (Aviara et al., 2006; Kaleemullah and Kailappan, 2004)

$$\text{MRE (\%)} = \frac{100}{N}\sum_{i=1}^{N}\frac{\left|M_i - M_{pi}\right|}{M_i} \quad \ldots(1)$$

$$\text{RMSE} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(M_i - M_{pi}\right)^2\right]^{1/2} \quad \ldots(2)$$

Where Mi is the ith experimental EMC value, Mpi is the ith predicted EMC value and N is the number of experimental data.

While the value of $r^2$ close to 1, and *that of RMSE close* to 0, indicate a better fit, MRE below 10 % appears to be indicative of a good fit for practical purposes (Lomauro *et al*., 1985). Regarding residual plot, acceptance of a model is based on its randomness, i.e., the data points tend to fall in a horizontal band around zero and showing no clear pattern.

*Net isosteric heat of sorption*

The net isosteric heat of sorption ($q_{st}$) was calculated from equation (3)

$$\ln a_w = -\frac{q_{st}}{RT} + z \quad \ldots(3)$$

where R is the universal gas constant, z is the integration constant and T is absolute temperature.

At any specific moisture content and using the best fit MSI curve, corresponding water activity values at three temperatures were determined. A regression line (ln $a_w$ versus 1/T) was drawn using these data (Kaymak-Ertekin and Gedik, 2004)), and $q_{st}$ was estimated from the slope of the straight line. This procedure had been repeated for other moisture contents. It is worth mentioning here that depending on the positive or negative sign of the slope, sign of $q_{st}$ will be either negative or positive. According to Kaymak-Ertekin and Gedik (2004), the sign of $q_{st}$ is purely a mathematical result and has no bearing with its physical interpretation. Thus, in this study only absolute values of $q_{st}$ were considered.

**Table 1**. Models fitted to the experimental data

| Model | Equation |
|---|---|
| GAB | $M = \frac{M_o C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$ |
| Peleg | $M = K_1 a_w^{n_1} + K_2 a_w^{n_2}$ |
| Modified Oswin | $a_w = \frac{1}{\left[\left\{(A + BT)M^{-1}\right\}^X + 1\right]}$ |

**Results and Discussion**

*Equilibrium moisture contents*

The mean EMC values of films along with their respective standard deviation are presented in Table 2. F-test was found to be significant at 1 % level amongst the mean EMC of different compositions as evident for any particular row, i.e., at definite $a_w$ and temperature. This table validates that the observed difference among treatment means is real, and incorporation of different antimicrobials exerts definite influence on the extent of water sorption. Comparing the LSD values (Table 2), it is also observed that all the pairs of EMC values, excepting those at 25°C between control and SP, for $a_w$ 0.237, and between PS and SP, for $a_w$ 0.528, are different at 1% or 5% level of significance.

*Fitting to sorption models*

The respective constants involved for each model (Table 1) and the errors terms (as mentioned above) have been presented in Tables 3-5. It is observed from the tables that all the residual plots for Oswin model followed random nature while that for GAB and Peleg models indicated random behavior only in around 40 % and 50 %, respectively, of the total isotherms. For all the three models: the value of $r^2$ was close to 1 for all the isotherms, while for 75 % of the isotherms MRE % was less than 10. The values of RMSE were in the range 0.366-1.968 (for GAB), and 0.128-1.966 (for Peleg). For modified Oswin, the range was relatively narrow spanning within 1.524-2.103. Modified oswin, therefore, was considered as the best model for the present study. According to Chen (2002), modified Oswin model but not the GAB model could be used to explain the sorption behaviour of high starch products.

**Table 2.** Equilibrium moisture content of edible film at different temperature and relative humidity

| Tempera-ture (°C) | Water activity | #EMC (% db)±SD | | | | LSD.01 | LSD.05 |
|---|---|---|---|---|---|---|---|
| | | Control | BA | PS | SP | | |
| 25 | 0.113 | 4.416± 0.491 | 5.917 ± 0.159 | 4.861 ± 0.115 | 3.190 ±0.297 | 0.831 | 0.571 |
| | 0.237 | 6.160*±0.018 | 6.056±0.024 | 6.599±0.010 | 6.135*±0.007 | 0.044 | 0.031 |
| | 0.327 | 7.590±0.016 | 8.015±0.009 | 8.219±0.005 | 10.203±0.002 | 0.027 | 0.018 |
| | 0.443 | 9.931±0.064 | 10.022±0.008 | 9.839±0.053 | 8.528±0.007 | 0.115 | 0.079 |
| | 0.528 | 12.101±0.003 | 12.559±0.250 | 11.135*±0.119 | 11.063*±0.221 | 0.485 | 0.333 |
| | 0.742 | 16.550±0.068 | 19.867±0.012 | 14.810±0.008 | 14.717±0.010 | 0.096 | 0.066 |
| | 0.752 | 25.101±0.010 | 21.478±0.003 | 19.539±0.026 | 21.585±0.004 | 0.038 | 0.026 |
| | 0.843 | 31.202±0.014 | 27.675±0.006 | 25.950±0.007 | 25.973±0.009 | 0.025 | 0.017 |
| 35 | 0.112 | 3.501±0.009 | 4.959±0.005 | 4.521±0.009 | 3.732±0.006 | 0.020 | 0.014 |
| | 0.215 | 8.149±0.007 | 7.530±0.005 | 6.111±0.008 | 5.895±0.009 | 0.020 | 0.014 |
| | 0.320 | 10.250±0.164 | 11.965±0.009 | 8.319±0.418 | 7.512±0.343 | 0.774 | 0.532 |
| | 0.436 | 12.102±0.155 | 10.309±0.229 | 10.799±0.274 | 8.760±0.323 | 0.693 | 0.476 |
| | 0.499 | 11.301±0.357 | 13.247±0.010 | 12.551±0.363 | 9.751±0.391 | 0.880 | 0.605 |
| | 0.720 | 15.059±0.050 | - | 16.899±0.009 | 17.633±0.010 | 0.090 | 0.059 |
| | 0.748 | 20.950±0.013 | 21.152±0.010 | 20.610±0.005 | 19.687±0.010 | 0.027 | 0.018 |
| | 0.829 | 28.499±0.012 | 28.149±0.008 | 31.105±0.015 | 29.913±0.008 | 0.031 | 0.021 |
| 45 | 0.111 | 2.889±0.012 | 4.296±0.014 | 4.929±0.005 | 4.819±0.006 | 0.028 | 0.019 |
| | 0.197 | 6.299±0.009 | 6.410±0.008 | 6.859±0.006 | 5.817±0.011 | 0.023 | 0.016 |
| | 0.311 | 9.220±0.011 | 7.946±0.008 | 7.381±0.006 | 7.611±0.013 | 0.027 | 0.019 |
| | 0.429 | 9.939±0.006 | 9.630±0.008 | 9.911±0.015 | 9.572±0.008 | 0.027 | 0.018 |
| | 0.469 | 11.181±0.009 | 10.201±0.005 | 11.679±0.005 | 12.012±0.011 | 0.022 | 0.015 |
| | 0.699 | 14.998±0.016 | 13.396±0.010 | 16.809±0.281 | 17.830±0.261 | 0.525 | 0.361 |
| | 0.745 | 21.950±0.169 | 20.757±0.312 | 23.820±0.465 | 22.979±0.393 | 0.965 | 0.663 |
| | 0.817 | 26.819±0.246 | 26.492±0.006 | 30.930±0.286 | 28.169±0.237 | 0.610 | 0.419 |

# Average of three replication. Treatment effect i.e., F test positive ($p<0.01$) for each row;*EMCs in a row are not significantly different.

**Table 3.** Estimated parameters and comparison criteria for GAB model

| Sample | Model Parameters | 25°C | 35°C | 45°C |
|---|---|---|---|---|
| Control | M0 | 6.164 | 6.405 | 6.573 |
| | C | 13.814 | 26.706 | 12.174 |
| | K | 0.956 | 0.927 | 0.929 |
| | r2 | 0.962 | 0.952 | 0.974 |
| | RMSE | 1.968 | 1.889 | 1.392 |
| | MRE (%) | 6.666 | 16.974 | 13.255 |
| | Residual Plot | Pattern | Pattern | Pattern |
| Potassium Sorbate | M0 | 5.528 | 5.680 | 5.850 |
| | C | 49.072 | 32.678 | 30.849 |
| | K | 0.930 | 0.982 | 0.995 |
| | r2 | 0.977 | 0.984 | 0.989 |
| | RMSE | 1.198 | 1.193 | 1.029 |
| | MRE (%) | 6.968 | 8.702 | 6.136 |
| | Residual Plot | Pattern | Pattern | Random |
| Benzoic Acid | M0 | 6.740 | 7.965 | 5.237 |
| | C | 17.655 | 16.441 | 50.115 |
| | K | 0.906 | 0.867 | 0.981 |
| | r2 | 0.995 | 0.984 | 0.973 |
| | RMSE | 0.642 | 1.145 | 1.339 |
| | MRE (%) | 6.336 | 8.150 | 10.011 |
| | Residual Plot | Random | Random | Pattern |
| Sodium Propionate | M0 | 6.233 | 5.086 | 6.800 |
| | C | 13.497 | 23.032 | 12.082 |
| | K | 0.905 | 1.001 | 0.938 |
| | r2 | 0.948 | 0.998 | 0.993 |
| | RMSE | 1.915 | 0.366 | 0.741 |
| | MRE (%) | 13.497 | 4.307 | 6.135 |
| | Residual Plot | Random | Pattern | Random |

**Table 4.** Estimated parameters and comparison criteria for Modified Oswin model

| Sample | Model Parameters | Values |
|---|---|---|
| Control | A | 10.913 |
| | B | 0.029 |
| | x | 2.015 |
| | $r^2$ | 0.990 |
| | RMSE | 2.103 |
| | MRE % | 12.711 |
| | Residual Plot | Random |
| Potassium Sorbate | A | 9.319 |
| | B | 0.068 |
| | x | 2.061 |
| | $r^2$ | 0.995 |
| | RMSE | 2.025 |
| | MRE % | 8.256 |
| | Residual Plot | Random |
| Benzoic Acid | A | 13.788 |
| | B | -0.048 |
| | x | 2.061 |
| | $r^2$ | 0.989 |
| | RMSE | 1.524 |
| | MRE % | 9.704 |
| | Residual Plot | Random |
| Sodium Propionate | A | 9.154 |
| | B | 0.060 |
| | x | 1.886 |
| | $r^2$ | 0.993 |
| | RMSE | 1.573 |
| | MRE % | 8.736 |
| | Residual Plot | Random |

**Table 5.** Estimated parameters and comparison criteria for Peleg model

| Antimicrobial added | Model Parameters | 25°C | 35°C | 45°C |
|---|---|---|---|---|
| Control | K1 | 53.240 | 117.607 | 67.437 |
| | n1 | 6.793 | 12.048 | 8.863 |
| | K2 | 16.340 | 18.298 | 18.337 |
| | n2 | 0.643 | 0.590 | 0.692 |
| | r2 | 0.962 | 0.975 | 0.980 |
| | RMSE | 1.966 | 1.337 | 1.194 |
| | MRE(%) | 7.995 | 12.718 | 10.678 |
| | Residual Plot | Random | Random | Random |
| Potassium Sorbate | K1 | 53.831 | 147.644 | 72.751 |
| | n1 | 8.677 | 12.559 | 7.052 |
| | K2 | 15.126 | 19.631 | 15.263 |
| | n2 | 0.542 | 0.718 | 0.520 |
| | r2 | 0.982 | 0.996 | 0.990 |
| | RMSE | 1.047 | 0.560 | 0.972 |
| | MRE(%) | 4.698 | 4.451 | 5.795 |
| | Residual Plot | Pattern | Pattern | Random |
| Benzoic Acid | K1 | 32.322 | 47.840 | 79.053 |
| | n1 | 3.259 | 7.792 | 8.595 |
| | K2 | 9.152 | 19.015 | 14.371 |
| | n2 | 0.230 | 0.572 | 0.512 |
| | r2 | 0.996 | 0.987 | 0.981 |
| | RMSE | 0.513 | 1.012 | 1.105 |
| | MRE(%) | 4.362 | 7.049 | 5.683 |
| | Residual Plot | Pattern | Random | Pattern |
| Sodium Propionate | K1 | 42.772 | 73.091 | 42.628 |
| | n1 | 7.701 | 7.753 | 5.378 |
| | K2 | 16.381 | 14.342 | 15.685 |
| | n2 | 0.648 | 0.593 | 0.578 |
| | r2 | 0.951 | 0.999 | 0.993 |
| | RMSE | 1.840 | 0.128 | 0.740 |
| | MRE(%) | 12.897 | 1.635 | 5.771 |
| | Residual Plot | Pattern | Random | Pattern |

*Sorption isotherms of SSEF*

Figures 1-7 show the predicted lines of sorption isotherms for different films at three temperatures using the modified Oswin model.

*Effect of antimicrobials on the MSI of the films*

The isotherms of control film and film containing different antimicrobials are shown in Figures 1, 2 and 3 for 25, 35, and 45°C, respectively. Irrespective of temperature, all the moisture sorption isotherms, have been found to be sigmoid in shape (type II according to BET classification)**;** the moisture content of the films increased slowly with increase in $a_w$ up to about 0.75, after which small increase in relative humidity lead to large adsorption of moisture - a typical characteristics of complex or polymeric materials (Coupland *et al*., 2000). This is attributed to physical adsorption of water molecules on micro-porous solid and leads to multilayer formation (Erbas *et al*., 2005). Therefore, adsorption of moisture for all the films proceeds with multilayer sorption mechanism, and the trend remained invariant to temperature and nature of antimicrobial incorporated.

In Figure 1 (for 25°C) the isotherms are clearly distinguishable compared to that of 35 °C (Figure 2) and 45°C (Figure 3). Figure 1 shows that at any water activity, films incorporated with benzoic acid possess higher moisture content than that of control or films incorporated with sodium propionate or potassium sorbate; the later two films showed lower moisture content than that of control almost over the entire range of $a_w$ values. It may be interesting to note that, at any temperature but at fixed water activity (<0.65), the film incorporated with potassium sorbate possess higher moisture content than the film containing sodium propionate, suggesting that the former film is more hygroscopic than the later. However, at $a_w$ values above 0.65-0.70, a cross over phenomena was observed. It may be that, at higher water activity (equilibrium relative humidity) more dissolution of sodium propionate salt occurs in the film with manifestation of higher adsorption of moisture than potassium sorbate; the later is more soluble than the former.

*Effect of temperature on the MSI of the film*

Effect of temperature on MSI for control film, and films with potassium sorbate, sodium propionate and benzoic acid are shown in Figures 4, 5, 6 and 7, respectively. In case of control film (Figure 4), at any particular water activity value, the film gradually adsorbs more moisture as the temperature increases from 25 to 45°C. Possibly, plasticized starch molecules easily undergo change in their orientation. This behaviour is facilitated further with the increase in temperature, and consequently there is exposition of more water binding sites in the starch backbone. In other words, at any particular moisture content, increase in temperature causes decrease in water activity of the films, suggesting opening up more new binding sites for water, and thus reduce the free energy of bound water (water activity). The same phenomenon was also observed for films containing potassium sorbate (Figure 5) and sodium propionate (Figure 6). For BA films (Figure 7), increase in temperature gradually decreases the moisture sorption – the trend common for biomaterials. Here it may be that though there is exposition of binding sites with rise in temperature, BA present in the system which is capable of forming hydrogen bonds on the water binding sites compete with water and preferentially get adsorbed. Such type of antithetic behavior in moisture sorption as observed for control, PS and SP films has been reported for food rich soluble solids and susceptible to structural orientation (Das *et al*., 2002; Rizvi, 1986).

*Net isosteric heat of sorption*

The variation in net isosteric heat of sorption ($q_{st}$) with moisture content (5 – 40 %, db) for SSEF, with and without antimicrobials is shown in Figure 8. The figure reveals that, irrespective of the nature of the film, $q_{st}$ decreased exponentially (equations 4-7) with the increase in moisture content.

$q_{st}$ = 4.2854 e-0.0684M ... (4), for control, $r^2 = 0.995$

$q_{st}$ = 7.4298 e-0.0701M ... (5), for benzoic acid, $r^2 = 0.993$

$q_{st}$ = 8.0327e-0.065M …(6), for sodium propionate, $r^2 = 0.986$

$q_{st}$ = 9.3304 e-0.0684M …(7), for potassium sorbate, $r^2 = 0.956$

where 'M' represents moisture content (%db) of the film.

According to Tsami (1991), for any absorbing surface higher the value of $q_{st}$, higher is the degree of binding. Therefore, this exponential relationship suggests that, in each of these films, binding sites are heterogeneous in nature.

The figure further reveals that, $q_{st}$ is lowest for control, followed by films containing BA, SP and PS, in the increasing order. Thus, addition of any of the antimicrobial agents increases the binding energy between water and the film surface, and the extent of increase is influenced by the nature of the additive. However, the difference in $q_{st}$ among the films disappears for moisture content around and beyond 40 % db. This type of converging behavior may be due to increased plasticization of the biopolymers

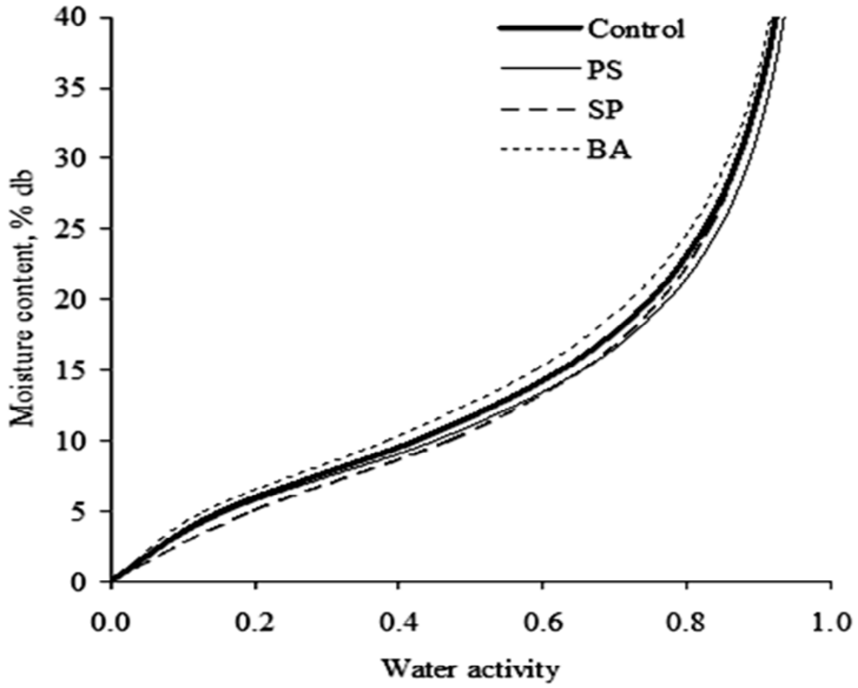


**Figure 1**. Effect of antimicrobials on moisture sorption isotherm of films at 25 °C.

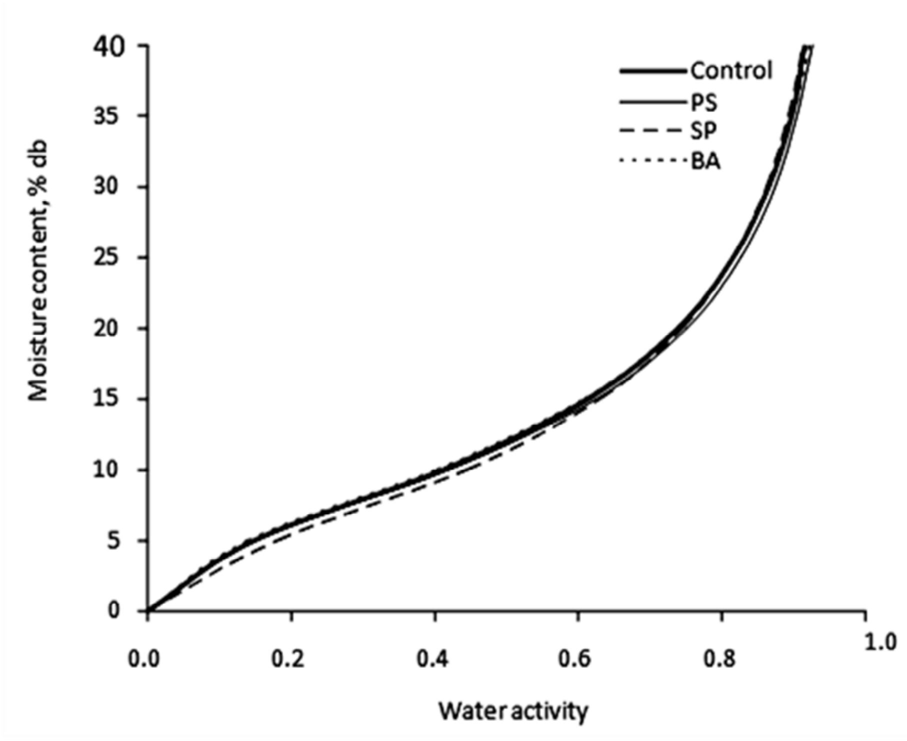


**Figure 2**. Effect of antimicrobials on moisture sorption isotherm of films at 35°C.

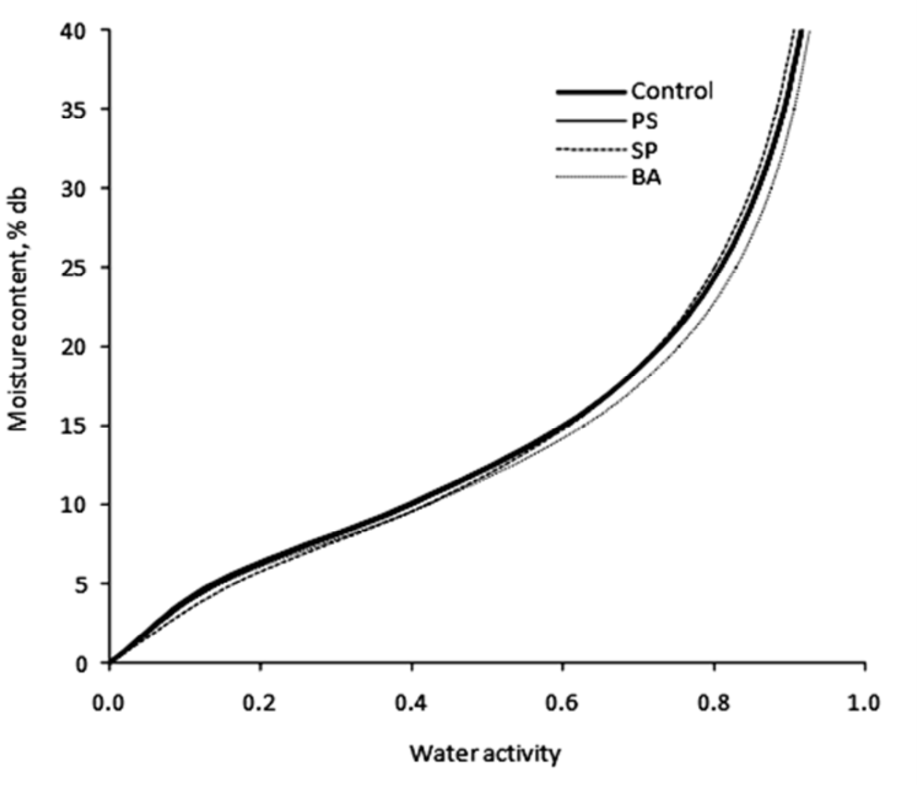


**Figure 3.** Effect of antimicrobials on moisture sorption isotherm of films at 45°C.

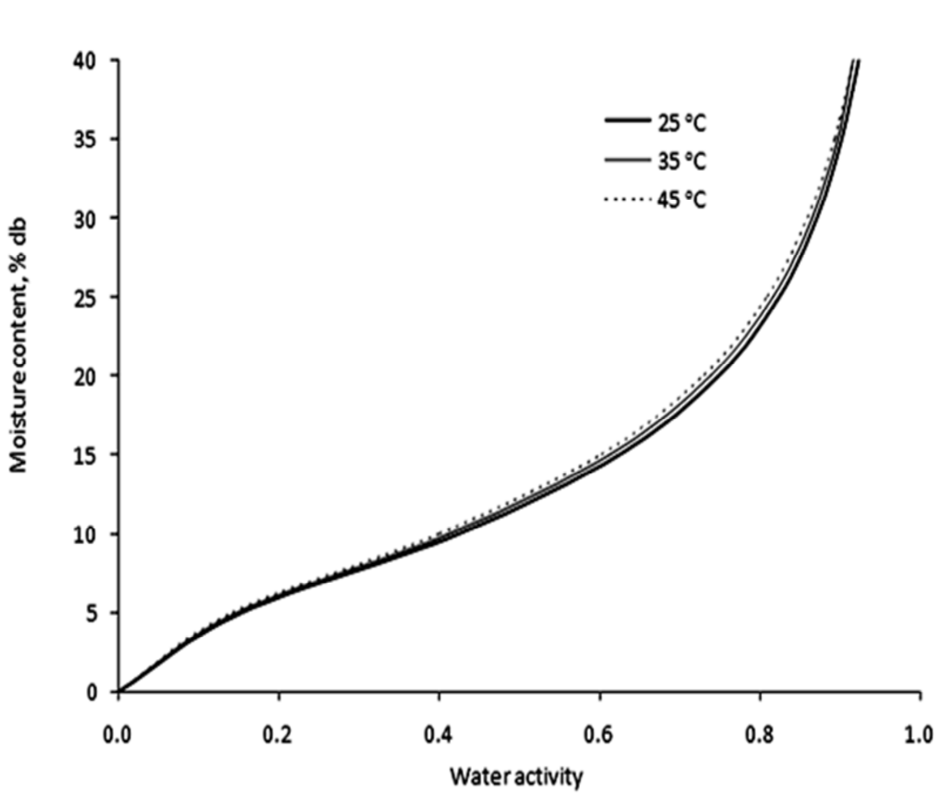


**Figure 4.** Effect of temperature on moisture sorption isotherm of control film.

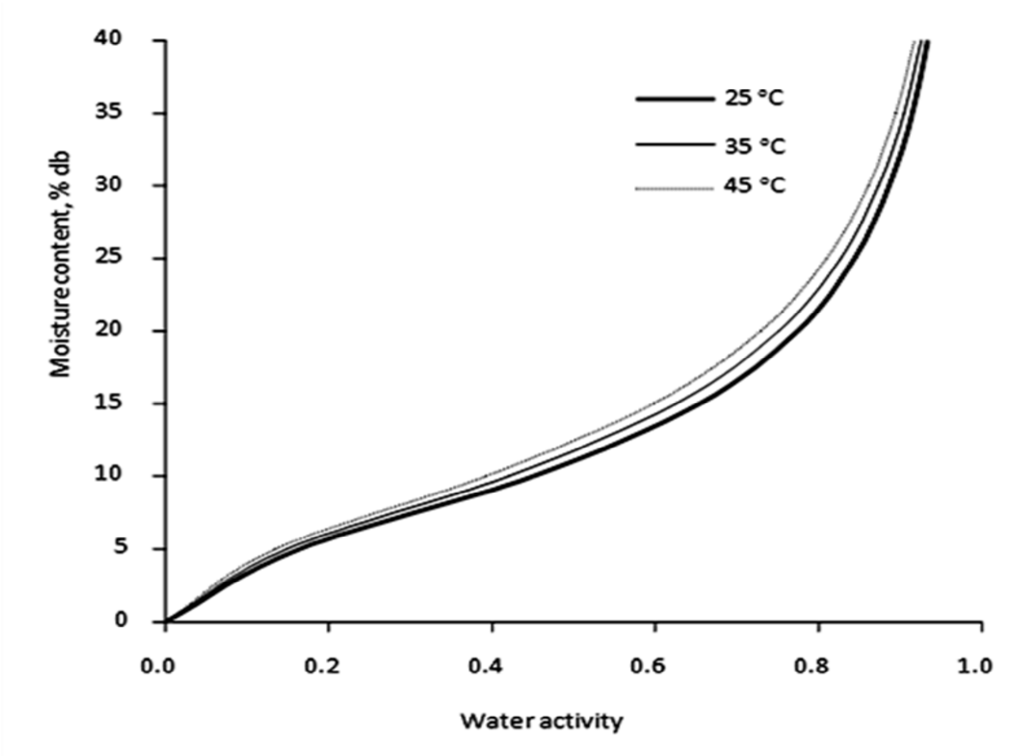


**Figure 5.** Effect of temperature on moisture sorption isotherm of potassium sorbate incorporated film

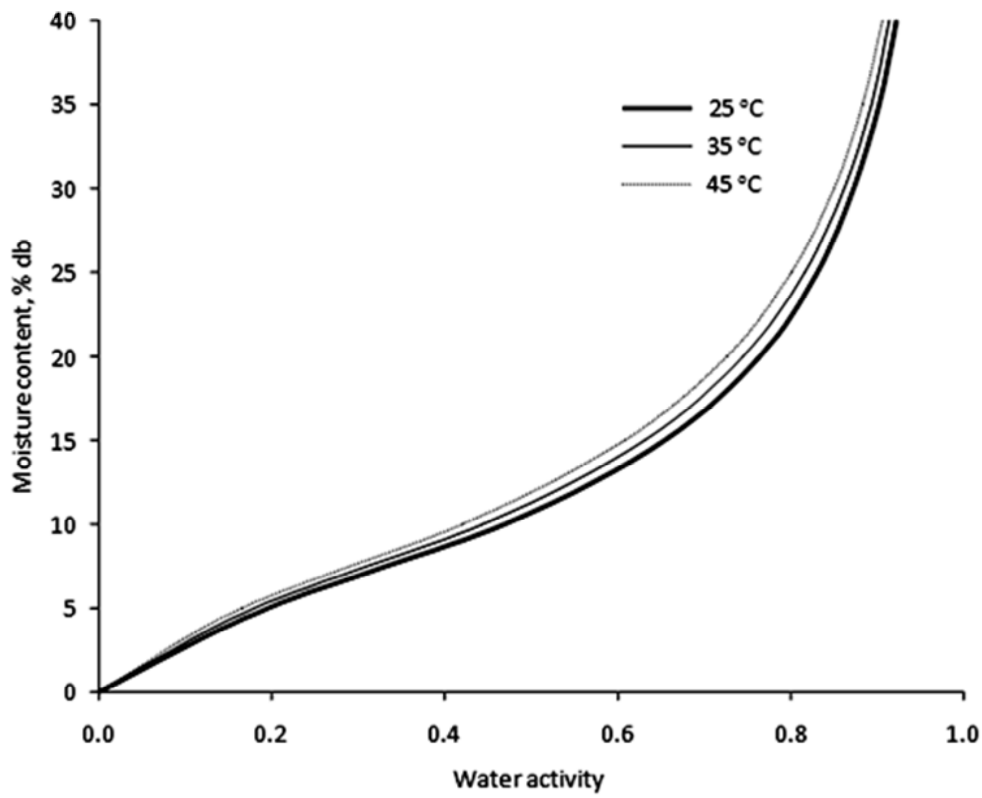


**Figure 6.** Effect of temperature on moisture sorption isotherm of sodium propionate incorporated film.

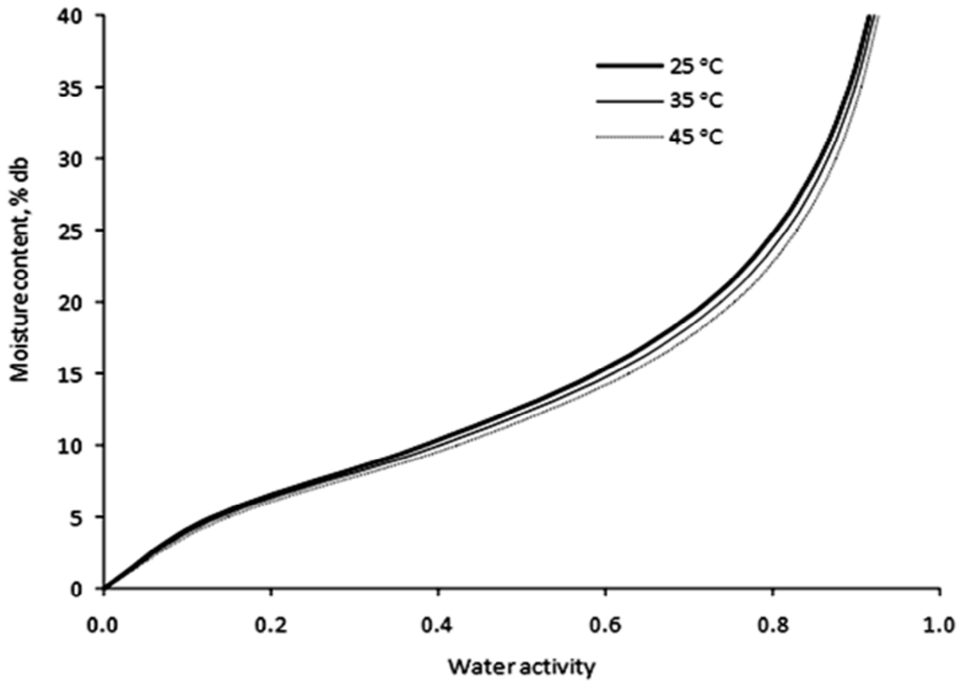


**Figure 7.** Effect of temperature on moisture sorption isotherm of benzoic acid incorporated films.

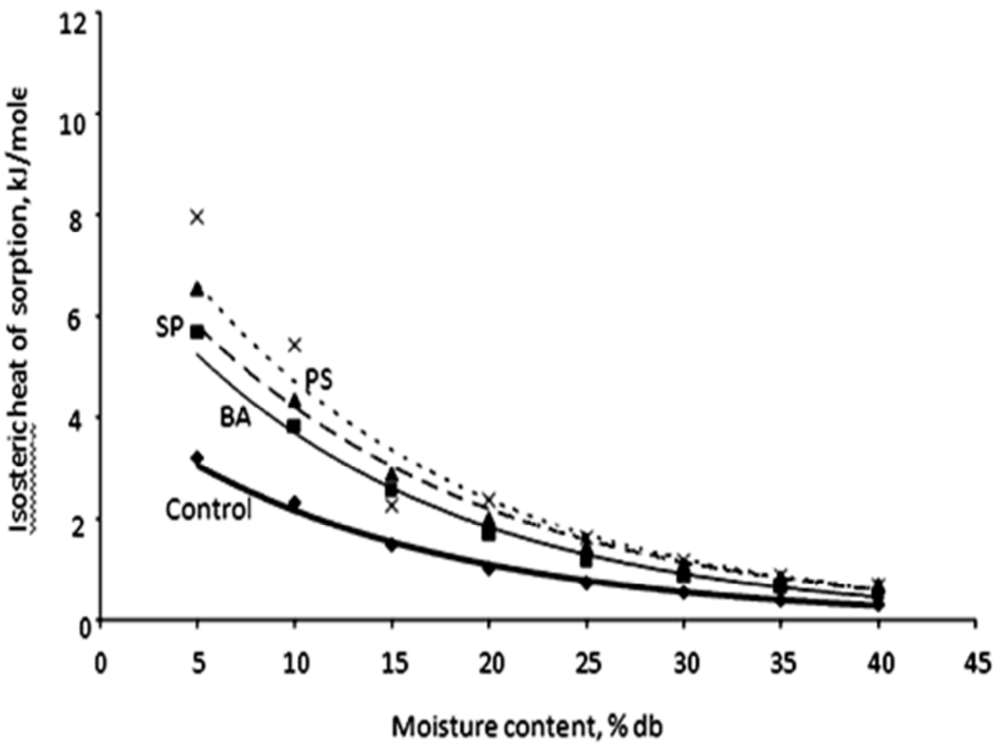


**Figure 8.** Behaviour of isosteric heat of sorption of starch based edible films at different moisture contents.

in the film at high moisture content (Gabas *et al*., 2007).

## Conclusions

MSI of edible starch films without any antimicrobial preservative and containing PS, SP, and BA followed type II BET isotherm and modified Oswin model fitted best to explain their sorption behaviour. Incorporation of these preservatives alters the MSI of the control film to a higher extent at 25°C compared to 35 and 45°C. At 25°C, at any water activity/relative humidity, moisture content of film containing BA is higher than that of control or films containing either SP or PS. For 25-45 °C and at any water activity ($a_w$<0.65), the PS incorporated film possess higher moisture content and thus is more hygroscopic than SP incorporated film, while at $a_w$ >0.65, a cross over phenomena has been observed.

For all relative humidities, moisture content increases with increasing temperature for the control films and films containing PS and SP; benzoic acid containing film exhibited a reverse effect. The net isosteric heat of sorption followed a negative exponential relationship with film moisture content and was minimum for control film followed by that of film containing BA, SP and PS, in that order. However, the difference in $q_{st}$ disappear when the moisture content of film is 40% db and above.

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