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Prediction of Sorption Characteristics by Mass Balance Concept

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함량비례 개념에 의한 수분흡습 특성의 예측

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Abstract

The water sorption isotherms of individual insoluble components of corn starch, isolated soybean protein (ISP) and casein and their binary mixtures of corn starch-ISP and corn starch-casein were measured and analyzed. BET monolayer values and Smith plot parameters from the results of sorption isotherms were calculated by mass balance concept. The comparisons between experimental and predicted values resulted in an error of 2.29% for equilibrium moisture content and an error of 2.95% in monolayer value for the mixture 50% corn starch- 50% ISP. On the other hand, for the mixture 50% corn starch-50% casein the errors were 2.66% and −5.34%, respectively.

Introduction

Each component has shown a specific characteristic in water sorption while fabricated food has shown a different curve of water sorption isotherm in relation to that of each component. Therefore, prediction of water sorption isotherms of food mixtures from the knowledge of the sorption characteristics of individual components would be valuable to predict the storage stability of such foods.

Serveral studies have been conducted to predict food products isotherms[1-4]. Iglesias[3] has tried to predict water sorption isotherms of binary mixtures from knowledge of composite isotherms cannot always be given as granted, but in the mixtures of 50% safflower protein-50% AVICEL, 50% safflower protein- 50% starch gel and 50% starch gel- 50% AVICEL the predicted equilibrium moisture contents by mass balance concept would be 'acceptable" and in none of those mixtures is the percentage difference in moisture content at any a higher than ±10%. Lang and Steinberg[4] has also studied to predict water activity of a multicomponent food formulation- that is, binary and ternary mixtures-with the their model equation derived from mass balance concept and Smith equation and reported that the equation could be shown to give excellent accuracy with the mixtures composed of starch, casein, sugar, soy flour, and salt. In the above two cases, they suggested that at a given a_w the moisture content of a mixture is equal to a weighted average of the moisture content of each component at that a_w, and concluded that each component sorbs water independently of the others in binary or ternary mixtures.

The purpose of the present work was to characterize the sorption properties of model food systems consisted of corn starch, ISP or casein, such as water sorption isotherm, BET monolayer value and specific parameters of the Smith plot, and to investigate the relation between the experimental and predicted values calculated by mass balance concept.

Materials and Methods

Materials

Ingredients studied were as follows: (1) corn starch, Sun-il brand (Sun-il Glucose Co., Inchon, Kyonggi-do, Korea) at 12.3% moisture, w.b.; (2) isolated soybean protein (ISP), Golden Cal brand (Golden Califonia Co., Supelveda, CA) at 6.1% moisture, w.b.; (3) casein, purified (Junsei Chemical Co., Tokyo, Japan) at 4.2% moisture, w.b.. Various salts used were extra pure or reagent grade. The composition of the mixtures studied, expressed on a wet basis, are shown in Table 1. These mixtures were mixed in a 4 quart Hobart mixer for 60 min. The bowl was covered with aluminium foil to prevent the loss of

Table 1. Composition of mixture studied

Mixture	Compsition, % with basis
A	100% Corn Starch
B	50% Corn Starch-50% ISP
C	50% Corn starch-50% Casein
D	100% ISP
E	100% Casein

small airborne particles[4]

Moisture determination

Moisture content was determined by the vacuum oven method[6] using 60°C and 29.8 in. Hg vacuum for 36*hr*. Determinations were made in triplicate.

Water sorption isotherms

Water sorption isotherms at 25°C of the model mixtures, were determined gravimetrically by placing 1-2g samples over various saturated salt solutions of known water activity. The a_w values for the saturated salt solutions were obtained directly from those reported by Rockland[7]. The values were : LiCl, 0.11; $K(CH_3COO)$, 0.23; $MgCl_2$, 0.33; K_2CO_3, 0.43; NaBr, 0.57; $CuCl_2$, 0.67; NaCl, 0.75 and K_2CrO_4, 0.87 at 25°C.

The saturation of samples was carried out in Modified Proximity Equilibrium Cell (MPEC), which is made of acryl resin, as referred by McCune *et al.*[8]. MPEC is consisted of upper cap and main body, in which they are separated about 1*mm* each other. This crack was enable to place a 55*mm* diameter Toyo #5A quantitative filter paper to support the sample and at the same time allow transmission of moisture. This is shown as a schematic in Fig. 1.

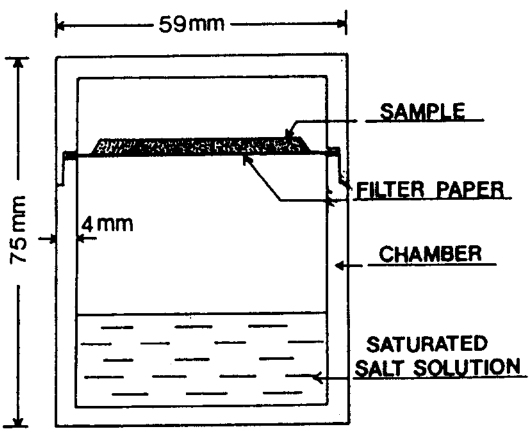

Fig. 1. Modified proximity equilibration cell for rapid equilibration of sample to saturated solution of a standard salt

Determination of monolayer value

The Brunauer-Emmet- Teller equation (BET equation) was used to determine the moisture content of monolayer[9] in each model systems and can be expressed as follows:

$$\frac{1}{m\,(1\text{-}a)} = \frac{1}{m_1 C} + \frac{C\text{-}1}{m_1 C}\,a$$

Where, a is water activity, m is water content (gH_2O/g solid), m_1 is the monolayer value, and C is a constant.

Determination of Smith plot parameter

A relation between water activity and moisture content for ingredients, Suggested by Smith[5], can be expressed as :

$$m = b \log (1\text{-}a_w) + a$$

Where, m is the moistue content, a_w is the water activity, a is the intercept on the mixture axis, and b is the slope of the regression line for the linear sorption isotherm.

Results and Discussion

MPEC was used to allow a more complete equilibration of the sample in the same equilibration time. MPEC was modified from the Proximity Equilibration Cells (PEC) and its effectiveness was studied by Lang et al.[10]. They reported that corn starch shows a consistently higher equilibrium moisture content (EMC) with the PEC and each a_w the difference was close to the mean of 6% in comparison of the EMC with the conventional desiccator. In practical use, MPEC was more convenient in handling samples than the PEC.

Fig. 2 shows the experimental sorption isotherms of the individual components and binary mixtures, such as corn starch, ISP, casein, 50% corn starch-50% ISP, and 50% corn starch-50% casein. The moisture content of ISP was found to be more dependent on the water activity than the other individual components. Water sorption

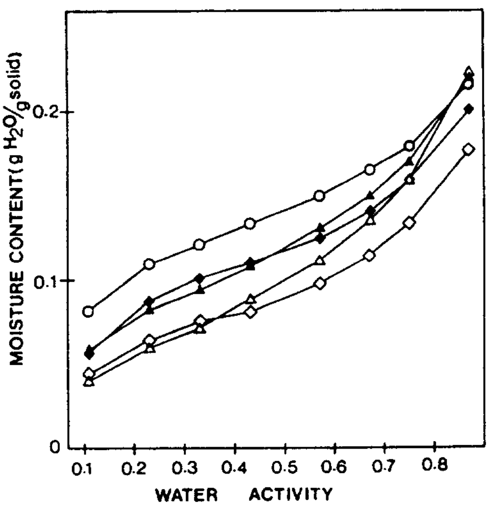

Fig. 2. Water sorption isotherms of individual components and binary mixtures at 25°C: (—○—) corn starch, (—△—) ISP, (—◇—) casein, (—▲—) 50% corn starch-50% ISP, (—◆—) 50% corn starch-50% casein.

isotherms of two binary mixtures was shown to be placed between those of two individual components composing each mixture.

Predicted value of EMC, monolayer value, and Smith plot parameters in any binary mixtures was calculated assuming that the amount of water sorbed at any relative humidity is derived by the weight percentage of each component times the amount it would sorb alone. From this mass balance concept,[3,4] it is defined as:

$$m_p = m_1X_1 + m_2X_2$$
$$m_{1p} = m_{11}X_1 + m_{12}X_2$$
$$a_p = a_1X_1 + a_2X_2$$
$$b_p = b_1X_1 + b_2X_2$$

Where, X_1, X_2 are weight fractions (wet basis) and m_1, m_2 are equilibrium moisture contents of component 1 and 2, respectively. m_{11}, m_{12} are BET monolayer values of each component, and a, b are Smith plot parameters of any component. Letter p means "predicted". The percent error between experimental (D_{exp}) and predicted data (D_{pre}) was calculated as:

Table 2. Comparioson of experimental and predicted equilibrium moisture contents for binary mixtures at 25°C

	Water activity	Moisture Content (gH_2O/gsolid)		
		Experimental	Predicted	Error (%)
Starch-ISP	0.11	0.058	0.061	+5.17
	0.23	0.082	0.085	+3.66
	0.33	0.094	0.097	+3.19
	0.43	0.108	0.111	+2.78
	0.57	0.131	0.131	0
	0.67	0.150	0.151	+0.67
	0.75	0.1790	0.169	-0.59
	0.87	0.220	0.225	+2.27
			Absolute mean error =	2.29
Starch-Casein	0.11	0.056	0.063	+12.50
	0.23	0.087	0.087	0
	0.33	0.101	0.099	-1.98
	0.43	0.110	0.108	-2.73
	0.57	0.125	0.124	-0.80
	0.67	0.141	0.141	0
	0.75	0.159	0.157	-1.26
	0.87	0.201	0.197	-1.99
			Absolute mean error =	2.66

$$\frac{D_{pre} - D_{exp}}{Dexp}(100) = \text{Error}$$

Table 2 shows a comparison between experimental and predicted

EMC at various water activities for two binary mixtures. This shows that using mass balance concept in 8 calculations of corn starch-ISP binary mixture resulted in a miximum error of only 5.17%. The absolute mean error was 2.29%, showing good agreement between the experimental and predicted EMC. Iglesias et al.[3] reported that for the mixture ISP-starch the maximum observed difference is EMC amounted to about 18%. The maximum error and absolute mean error for the mixture corn starch-casein were 12.5% and 2.66%.

By the above results, it seems that the mass balance concept was better applied to predict the sorption behavior of the mixture corn starch-ISP compared with the mixture corn starch-casein.

Fig. 3 shows Smith plot of the regression lines for the linear sorption isotherm at 25°C over a_w 0.33-0.87 for two binary mixtures.

The BET monolayer values and Smith plot parameters were calculated from the water sorption isotherms in Fig. 2, and predicted data were also calculated from the sorption behaviors of individual ingredient by mass balance concept. These values are shown in Table 3. The percent error between experimental and predicted monolayer

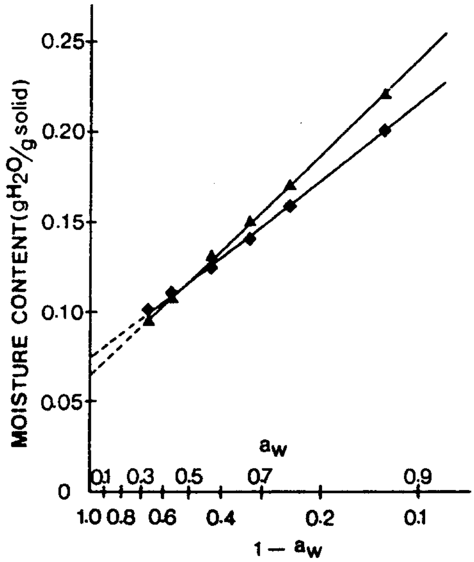

Fig. 3. Regression lines for the linear sorption isotherm at 25°C for binary mixtures over a_w 0.33-0.87: (—▲—) 50% corn starch-50% ISP, (—◆—) 50% corn starch-50% casein

Table 3. Comparison of experimental and predicted BET monolayer value and Smith plot parameters of model mixtures at 25°C

	Parameters*	Experimental	Predicted	Error(%)
Starch	m_1	0.0786		
	a	0.1021		
	b	-0.1291		
Starch-ISP	m_1	0.0645	0.0664	+2.95
50:50	a	0.0650	0.0664	+2.15
	b	-0.1753	-0.1762	+0.51
Starch-Casein	m_1	0.0674	0.0638	-5.34
50:50	a	0.0749	0.0743	-0.80
	b	-0.1407	-0.1375	-2.27
ISP	m_1	0.0542		
	a	0.0306		
	b	-0.2232		
Casein	m_1	0.0490		
	a	0.0464		
	b	-0.1458		

*m_1: BET monolayer value, a: intercept, b: slope

value is 2.95% for starch-ISP and −5.34% for stach-casein. The error in a of Smith plot is 2.15% for starch-ISP and −0.80% for starch-casein, while in b the error is 0.51% for starch-ISP and −2.27% for starch-casein. With these results we could arbitrarily accept as a maximum permissible error in determination of sorption behaviors a value ±10% as described by Iglesias[3]. On this point, it is possible to say that the agreement between experimental and predicted sorption behaviors would be "acceptable" for these two binary mixtures. That is, none of percentage error in two binary mixtures is higher than ±10%.

As shown in Table 3, slope b parameter of starch, ISP, and casein was −0.1291, −0.2232, and −0.1458, respectively. Lang and Steinberg[11] reported that slope b of each component at 20°C over a_w 0.33-0.95 was −0.1485, −0.1728, respectively. These disagreements of slope b appear to be due to the difference of water activity in plotting and the experimental temperature. The absolute value of slope b was known to be indicative of humectant properties of the component[11].

Conclusion

The water sorption isotherms of binary mixtures were measured by using the Modified Proximity Equilibrium Cell and analyzed by mass balance concept. The comparisons between experimental and predicted values resulted in an error of 2.29% for equilibrium moisture content and an error of 2.95% in monolayer value for the mixture 50% corn starch −50% ISP and for the mixture 50% corn starch −50% casein the errors were 2.26% and −5.34%, respectively.

요　　약

二相混合物의 평형수분함량, 단분자층수분함량, Smith 방정식의 절편 a와 기울기 b를 예측하고자 "성분의 함량비례개념"을 이용하였다. 50 : 50인 옥수수전분과 분리대두단백의 二相混合物의 경우 평형수분함량은 절대오차평균이 2.29%이었으며, 단분자층수분함량은 2.95%, Smith 방정식의 a値는 2.15%, b値는 0.51%의 오차를 나타내었다. 반면 50 : 50의 옥수수전분과 카제인으로 제조한 二相混合物은 평형수분함량은 2.66%, 단분자층수분함량은 −5.34%, a値는 −0.80%, b値는 단지 −2.27%의 오차를 보이고 있어 "성분의 함량비례 개념"에 의한 二相混合物의 수분흡습특성 예측은 가능한 것으로 나타났다.

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