

THE EFFECT OF SUCROSE AND SODIUM CHLORIDE ON DESORPTIONAL BEHAVIORS OF HYDRATED AND GELATINIZED CORN STARCHES

HİDRATE NIŞASTA VE JELLERİNİN DESORPSİYON İZOTERMLERİNE SAKAROZ VE SODYUM KlorÜRÜN ETKİSİ

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ÖZET: Hidrate nişasta ve jellerinin desorpsiyon izotermi üzerine sakaroz ve sodyum klorürün etkisi statik gravimetric yöntem ile belirlenmiştir. Deneysel 25 ve 35°C sıcaklıkta ve 0.11-0.75 su aktivitesi aralığında yapılmıştır. izoterm verilerinin BET, GAB, geliştirilmiş BET, Halsey, Henderson, Oswin ve Smith eşitliklerine uyumu incelenmiştir. Belirtilen izoterm eşitliklerinin çalışılan a_w aralığında tüm örneklerdeki desorpsiyon verilerini açıklayamadığı görülmüştür. GAB ve geliştirilmiş BET eşitliğinin 0.11-0.75 su aktivitesi aralığında sakaroz içeren ve içermeyen hidrate veya jelatinize nişasta örneklerine ait desorpsiyon verilerine uyum sağladığı belirlenmiştir. Sakaroz-nişasta - su ve sodyum klorür-nişasta -su sistemlerinde bileşen etkileşimleri araştırılmıştır. Sakaroz-nişasta ya da sodyum klorür-nişasta etkileşimi desorpsiyonda meydana gelen düşmenin ölçülmesi ile belirlenmiştir. Hidrate nişastalarda her bir bileşenin desorpsiyon davranışının a_w ye bağımlı olduğu, nişasta ve sakaroz ya da sodyum klorür arasında bir etkileşimin olmadığı belirlenmiştir. Jel matrisinde ise polimer-çözünen madde etkileşiminden dolayı denge nem miktarının düştüğü belirlenmiştir. izoterm verileri Clasius-Clapeyron eşitliğinin integrale formunda değerlendirilerek örneklere ait net isosterik desorpsiyon ısıları hesaplanmıştır.

ABSTRACT: Desorption isotherms of hydrated corn starch and their gels containing sucrose or sodium chloride were determined by using the static gravimetric method. Experiments were carried out at 25°C over a water activity range of 0.11-0.75. BET, GAB, Halsey, Henderson, modified BET, Oswin and Smith equations were tested to fit the experimental moisture sorption data. None of the equations were found to be satisfactory to represent the desorptional data for all samples over this a_w range. The GAB and the modified BET equations fitted the data for hydrated and gelatinized starches with or without sucrose in the a_w range of 0.11-0.75. Component interactions in the sucrose-starch-water and sodium chloride-starch-water systems were investigated. Sucrose-starch or sodium chloride-starch interaction was determined by measuring the reduction in water desorption as compared to theoretical. The desorptional behaviors of each component in the hydrated starches depended on the a_w and no interaction was detected between starch and sucrose or starch and sodium chloride. In the gel matrix, however, equilibrium moisture contents decreased due to the polymer-solute interaction. Net isosteric heats of moisture desorption were estimated from equilibrium sorption data, using the integrated form of the Clasius-Clapeyron equation.

1. INTRODUCTION

The desorptional moisture content versus water activity at constant temperature is known as the desorption isotherm and the desorptional properties of foods can be best represented by it. Several factors such as composition, physical structure (e.g. crystalline or amorphous), temperature and the presence of solutes affect the equilibrium moisture content as well as the shape of the isotherm. Starch is the basic biopolymer of several foods and food products, which can be used as model material in investigation of desorptional characteristics. The interactions between starch and solutes (non-ionic such as sucrose and ionic such as sodium chloride) influence the desorptional equilibrium. Previous works on the effects of sucrose and sodium chloride on the desorptional characteristics of the polymer has been reported (SPIES and HOSENEY, 1982, CHINACHOTI and STEINBERG, 1984, CHINACHOTI and STEINBERG, 1984, CHINACHOTI and STEINBERG, 1986a-b). But their data were obtained at only one temperature, representing normal storage conditions. However, sorption properties at different temperatures are essential for modeling drying and

storage stability of dehydrated foods. In this research, we aim to determine the desorption isotherms of hydrated and gelatinized starches in the presence of sucrose or sodium chloride at 25°C and 35°C, and demonstrate the applicability of some well know sorption equations to the experimental results.

2. MATERIALS AND METHODS

Native corn starch was used in the experimental measurements and the following samples were prepared: hydrated starch (HS), sucrose containing hydrated starch (HSS), sodium chloride containing hydrated starch (HSC), gelatinized starch (GS), sucrose containing gelatinized starch (GSS) and sodium chloride containing gelatinized starch (GSC). Starch was denoted by Cargil Tarım Sanayi Ticaret A.Ş. İstanbul, Turkey and sucrose and sodium chloride were from Merck. The preparation of the samples was described elsewhere (UZMAN and ŞAHBAZ, 2000). Initially the HS and GS samples contained 60% and 13 % starch by weight, respectively. The HSS contained 46% starch and 14% sucrose (or sodium chloride), and GSS 9 % starch and 4 % sucrose (or sodium chloride). The gravimetric method proposed by GAL (1975) was adopted for this study and sorption experiments were described by UZMAN and ŞAHBAZ (2000) in detail.

3. RESULTS and DISCUSSION

The experiments were run in duplicate and the arithmetic mean value of equilibrium moisture content (emc) was used in the evaluation. Figs 1 and 2 showed the desorption isotherms of HS, HSS, GS and GSS at 25°C and 35°C. The desorption isotherm had three zones (Fig 1). In the first zone of the isotherm ($a_w < 0.1$) there was a rapid increase in the moisture content with a_w . In the second zone ($0.1 < a_w < 0.6$), the emc increased almost linearly and in the last zone ($a_w > 0.6$), higher increase in emc was noted. The desorption isotherms of GS were similar to those of HS in shape and have zones I-III in the same a_w interval and zone II as the widest (Figs 1 and 2). The sorption isotherms of sucrose and high sugar containing foods which are not rich in polymeric materials are of J type (FENNEMA, 1996). This behavior can be seen from the desorption isotherm of sucrose in Fig 1. HSS and GSS, on the other hand, exhibited S-type isotherms of type II, similar to those of HS and GS. The presence of sucrose in the mixtures caused a decrease in emcs of HS and GS, but did not affect the shape of the isotherms significantly. The only difference was the flattening of Zone II, especially noted in GS (Fig 2).

The water binding groups in starch granul are the hydroxly groups. Water molecules at the second zone of the isotherm binds to hydroxly groups and also associates with neighboring water molecules via the hydrogen bonds. This zone is wider than the first and the third ones due to the presence of hydroxyl groups in starch, capable of forming hydrogen bonds with water. In the third zone the biomatrix swells as a result of high moisture content and water is condensed in the

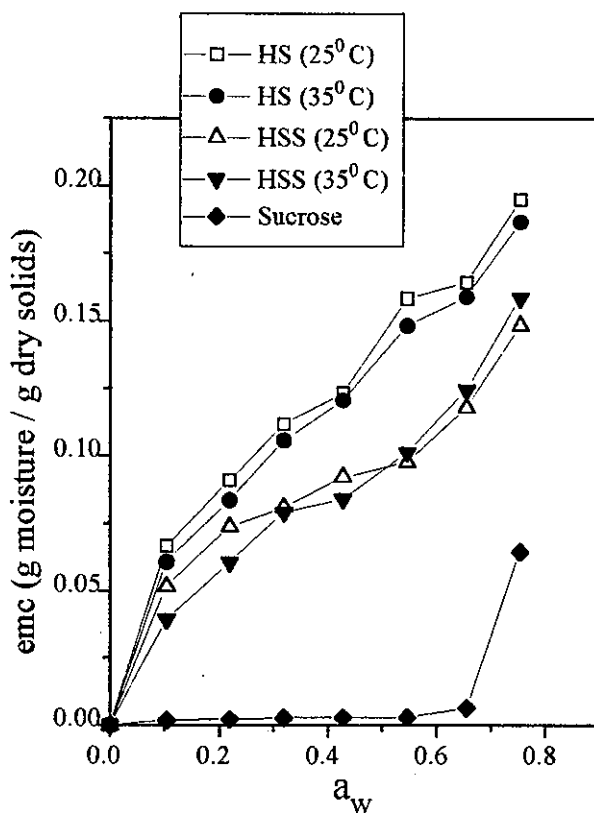


Figure 1. Desorption isotherms of hydrated starches (HS: hydrated starch; HSS:HS with sucrose)

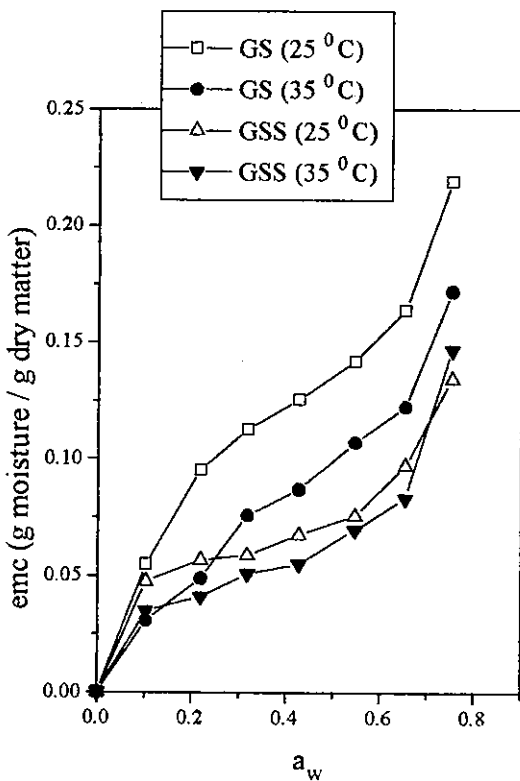


Figure 2. Desorption isotherms of gelatinized starches (GS: gelatinized starch, GSS: GS with sucrose)

sharp decrease in moisture content to zero due to sucrose crystallization (Figure 1). In this research, due to mold growth at $a_w > 0.75$, no data could be obtained at a_w s higher than this and the sharp decrease in moisture content could not be observed. But still the decrease in moisture content of sucrose was noted at a_w s lower than 0.75 (Fig 1). This means that the contribution of sucrose to emc was negligible below this a_w . Therefore the decrease in emc in the presence of sucrose was an expected results, since emc was given as gram moisture per gram of dry matter and the percent of starch in dry matter decreased to 77 % in HSS and to 69 % in GSS. Also in hydrated starch besides water, granules are readily penetrated by sucrose (molecular weight less than 1000) (HOSENEY, 1990). During gelatinization, sucrose binds to starch from the amorphous regions (SPIES and HOSENEY, 1982). Both phenomena might affect the binding of water molecules to starch and in turn reduced the emcs.

BAKHIT and SCHIMIDT (1992) determined the adsorption isotherm of NaCl over the a_w range of 0.23-0.93. They showed that the NaCl had negligible water sorption capacity at all a_w s below 0.75 and high water sorption capacity at a_w s higher than 0.75. Since NaCl dissolves and dissociates into its component ions above this value, the term "free NaCl" should be used for $a_w \geq 0.75$, indicating the presence of Na^+ and Cl^- ions. In the biomatrix, NaCl can be found in four different physical states, crystalline, amorphous, bound and dissolved. At a_w s below 0.75, bound and crystalline NaCl are in equilibrium (GAL, 1975). So the desorption isotherms of NaCl containing hydrated or gelatinized starches should be evaluated, depending on the a_w of the matrix. The isotherms, presented in Figure 3 displayed the typical sigmoid shape but similar to the sorption isotherm of NaCl their sorption properties changed at $a_w = 0.75$. A 3 fold increase in equilibrium moisture contents was

pores. Similarly the hydroxyl groups and the porous structure in the gel are the main factors effective on desorption. Starch gels are in metastable equilibrium. As a results of progressive aggregation and recrystallization of the polymer chains, time-temperature-dependent changes in gel structure may take place. Starch gels undergo changes in their crystallinity and water holding capacity on aging. As the gel ages, starch chains tend to interact with each other and thereby force water out of the system. This is called syneresis. Since the gelatinized starch reached the equilibrium in two or three weeks time, syneresis took place. So the syneresis also should be considered as another factor determining the emcs of the gelatinized starches. The desorption isotherms of HS and GS were found to be in good accordance with the related literature (IGLESIAS et al., 1980, IGLESIAS and CHIRIFE, 1982, BOKI et al., 1989, BOKI and OHNO, 1991).

The addition of sucrose changes the composition of the biomatrix. On desorption, the sucrose solution lost its water as a_w decreased to 0.86 (CHINACHOTI and STEINBERG, 1986a-b). Further decrease in a_w below 0.86 resulted in a

observed in hydrated samples and it was 4-6 folds in gelatinized ones. This tremendous increase is due to the dissolution of NaCl into its ions and at $a_w \geq 0.75$, NaCl is the component effective on desorptional equilibrium. Below this a_w , the equilibrium moistur contents of hydrated starches with or without NaCl (Figs 1 and 3) were found to be nearly the same. Considering that the hydrated mixture contained 77% starch by weight, our experimental result can be explained, based on the premise, that either the NaCl in the mixture possesses contribution on the sorption and/or Na^+ and Cl^- ions penetrate the starch granule and thus expose new binding sites for sorption. However, lower moisture contents were noted for the gelatinized starch with NaCl (Figs 2 and 3), due to the intreaction between starch and NaCl in the gel matrix. CHINACHOTI and STEINBERG (1985) described this interaction as nonionic polymer and ionic solute interaction which prevented the water binding to the sorption sites of starch.

BET, GAB, Halsey, Henderson, modified BET, Oswin and Smith equations were tested to fit the experimental data. Modeling was performed by using nonlinear regression program (SPSS for windows Release 5.0.1). The isotherm equation with a % RMS (root mean square) value was less than 10 was

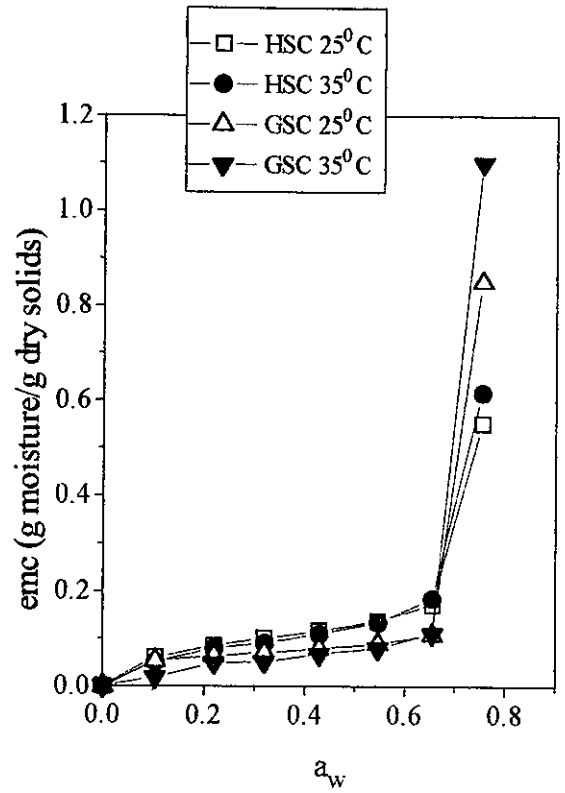


Figure 3. Desorption isotherms sodium chloride cohntaining hydrated starch and their gels (HSC: HS with sodium chloride, GSC: GS with sodium chloride)

Table 1. Applicability of GAB and Modified BET Equations to Isotherm Data ($a_w = 0.11-0.75$)

Equation	Temperature	Parameter	HS	GS	HSS	GSS
GAB	25°C	X_m	0.11	0.10	0.06	-0.04
		C	18.1	15.4	60.6	0.98
		k	0.7	0.7	0.8	43.8
		%RMS	3.0	6.8	5.7	5.8
	35°C	X_m	0.11	0.08	0.06	-0.31
		C	15.6	6.5	15.1	1.0
		k	0.6	0.8	0.8	110.7
		%RMS	2.8	6.0	5.0	7.2
Modified BET	25°C	X_m	0.10	0.11	0.07	0.06
		C	20.4	12.1	28.6	21.2
		%RMS	6.0	7.2	4.7	7.6
		X_m	0.10	0.09	0.08	0.07
	35°C	C	17.2	4.6	9.1	3.6
		%RMS	6.0	5.9	3.5	19.4

considered to be a good fit (MOK and HETTIARACHCHY, 1990, YANNIOTIS et al., 1990). Since the sorptional properties of NaCl changed tremendously at $a_w = 0.75$, none of th equations was satisfactory over this a range.

Based on % RMS values, GAB and modified BET equations were good fits with some exceptions (Table 1). The GAB equation did not fit the experimental data for GSS at both temperatures and modified BET equation had a RMS of 19.4 % for the same sample at 35°C. AGUERRE et al (1989) evaluated 74 experimental food isotherm by the modified BET equations and found that about 77% of th isotherms represented principally by starchy foods, proteins and spices obeyed

to the modified BET Equation I. From this point of view, our results were in good accordance with those reported. The parameter constants for GAB and modified BET equations were given in Table 1.

The net isosteric heat of sorption, ΔH_s , was calculated by using the integrated form of Clausius - Clapeyron equation (IGLESIAS and CHIRIFE, 1982). The ΔH_s varied between (29.0) - (-3.1) kJ/mol for hydrated starches and (116.9) - (-0.1) kJ/mol for gelatinized ones. High sorption energies indicated that Besides physical desorption, chemisorption was also observed in gelatinized samples at low moisture contents. Negative ΔH_s values were noted in HSS and GSS samples at high moisture contents. This was due to an increase in the solubility of sucrose in water above a_w of 0.6. Since this process is known to be endothermic, more sugar was being dissolved and thus more water was being held by the matrix at higher temperature. Also the moisture contents of HSC and their gels increased with increasing temperature at $a_w = 0.75$. In the GSC samples, higher increase with the temperature was noted. The slight increase in the solubility of NaCl with temperature may affect the moisture content of the starch matrix. At $a_w > 0.75$, NaCl in the biomatrix may exist in different forms, namely bound and dissolved, in equilibrium with each other (GAL, 1975). Therefore it may be considered at the equilibrium shifted to the dissolved NaCl side as the temperature increased and thus higher amounts of water are bound by the dissolved NaCl.

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