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## Heat of sorption and free energy change of freeze-dried pineapple pulp<sup>1</sup>

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### ABSTRACT

Two thermodynamic properties, the heat of sorption ( $Q_s$ ) and the Gibbs free energy change ( $\Delta G$ ) were evaluated at several temperatures (5, 25, 30, 35 and 55°C) on freeze-dried pineapple pulp. It was found that 1) the heat of sorption follows the Clausius-Clapeyron relationship; 2) the shape of the heat of sorption vs. the equilibrium moisture content curve was sigmoid; 3) the heat of sorption from adsorption data gave higher values than those from desorption data; and 4) the free energy change ( $\Delta G$ ) is linearly related to the equilibrium moisture content. These two parameters are very important in dealing with food stability because it is possible to predict the water activity at any given temperature of either of these values is known.

### RESUMEN

Calor de sorbición y cambio en energía libre en pulpa de piña liofilizada

Das propiedades termodinámicas, el calor de sorción ( $Q_s$ ) y el cambio en energía libre de Gibbs ( $\Delta G$ ) fueron evaluadas a diferentes temperaturas (5, 25, 30, 35 y 55°C) en pulpa de piña liofilizada. Se encontró que: 1) el calor de sorbición sigue la relación de Clausius-Clapeyron; 2) la forma de la curva que representa la relación de calor contra humedad es sigmoide; 3) los calores de sorbición obtenidos de los datos de adsorción son más altos que los obtenidos de los datos de desorción; 4) los cambios en energía libre están linealmente relacionados con el contenido de humedad en equilibrio. Estos dos parámetros son muy importantes cuando se estudia la estabilidad de un alimento, ya que conociendo el valor de cualquiera de ellos es posible predecir la actividad de agua a cualquier temperatura.

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## INTRODUCTION

Pineapple pulp can be used as a base for food products such as jellies, pie fillings and ice cream toppings. Other uses include dehydrated pulp mixed with other powdered ingredients to obtain products such as drink and cake mixes. The possibility of using dried pineapple pulp in new food products has made necessary the study of its stability and moisture sorption kinetics. One important parameter associated with stability and moisture sorption process is water activity. Hence it is important for food processors to predict water activity values in different conditions. A plot of the natural logarithm of water activity against the reciprocal of absolute temperature at constant moisture content generally will give a straight line. The slope of this line is equal to  $Q_s/R$ , where  $R$  is the gas constant and  $Q_s$  is the net isosteric heat of sorption (kJ/mole) defined as the difference between the total molar enthalpy change ( $\Delta H_{tot}$ ) and the molar enthalpy of vaporization ( $\Delta H_{vap}$ ).  $Q_s$  represents the binding energy of sorption.

$Q_s/R$  is expressed either as:

$$\frac{d(\ln a_w)}{d\left(\frac{1}{T}\right)} = \frac{Q_s}{R} \quad [1]$$

or by using two temperatures ( $T_1, T_2$ ) and the respective water activity ( $a_{w1}, a_{w2}$ ) as:

$$\ln \frac{a_{w2}}{a_{w1}} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad [2]$$

On the other hand, a plot of the natural logarithm of partial pressure of water in food against the reciprocal of absolute temperature will give a straight line, where the slope is  $\Delta H_{tot}/R$ .  $\Delta H_{tot}$  is the molar enthalpy of vaporization plus the molar heat of sorption. The mathematical expression for this relationship is:

$$\frac{d(\ln P)}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_{tot}}{R} \quad [3]$$

Equations [1] to [3] are all forms of the Clausius-Clapeyron equation and provide useful information on the binding energy of water molecules. Typically, maximum energy of binding occurs at a moisture content which corresponds to the monolayer value ( $m_o$ ) as determined from the

BET (Brunauer-Emmet-Teller) isotherm equation and is generally around an  $a_w$  of 0.2-0.4 (8). This is the moisture content at which each polar and ionic group has a water molecule bound to it which forms the start of a liquid phase. The monolayer value has been shown to correspond to the moisture content at which many food systems have the maximum stability in regard to chemical reactions. The BET theory predicts a constant heat of sorption until equilibrium moisture content reaches the monolayer value. When the monolayer value is reached, the heat of sorption falls to a low value (8). This indicates reduced water interactions (less binding energy). Experimental results on food systems follow the above behavior, but the transition from a high heat of sorption to a lower heat is not as predicted by BET. This has been documented by Henderson (6), Lima and Cal-Vidal (9), Roman et al. (12), and DeGois and Cal-Vidal (4).

Another thermodynamic approach to characterize the sorption phenomena is to analyze the Gibbs free energy. Previous works on this subject include those by Chung and Pfof (2, 3), Rockland (10), Rockland and Nishi (11), and Kumar (7). This thermodynamic parameter is defined as the work done by the attractive forces during sorption (2) and, in general, the model used to predict the change is:

$$\ln(-\Delta G) = \eta \times X + K \quad [4]$$

where,  $-\Delta G = R \times T \times \log(a_w)$ ,  $X$  is the equilibrium moisture content (kg water/100 kg dry solids),  $\eta$  and  $k$  are constants.  $\Delta G$  is the change in free energy between pure liquid water at temperature  $T$  and the water adsorbed by the pineapple pulp.

The purpose of this study was to measure the heat of sorption and the free energy change in freeze-dried pineapple pulp at different moistures since, by knowing the values of either of them, it is possible to predict the water activity at any given temperature. It is worth mentioning that there are no standard tables of heat of sorption or free energy for many foods, especially those processed by new technologies such as freeze-drying.

#### MATERIALS AND METHODS

Pineapple pulp was collected from a local pineapple manufacturer (Lotus, Land Authority of Puerto Rico, Barceloneta, Puerto Rico) where the main pineapple products are slices, chunks and juice. The pulp comes from the centrifugation stage in juice production. The pulp was frozen to  $-5^\circ\text{C}$  to reduce enzymatic activity and fermentation.

Slices of frozen pineapple 1.0 cm thick were placed in a Dura Stop Freeze Dryer (FTS System, Inc., New York, N.Y.)<sup>4</sup>. The dried pulp was comminuted and the powdered product was used in sorption tests.

Sorption measurements were made at different temperatures (5 to 55°C) and water activity levels (0.11 to 0.97). These levels were controlled by using preselected saturated salt solutions in glass desiccators according to Wolf et al. (13) where microcrystalline cellulose (Avicel pH 101, FMC, New York, NY)<sup>4</sup> is the reference material for the determination of sorption isotherms.

To determine the moisture content, samples of 10 g freeze-dried pineapple pulp were dried in a vacuum oven, where the pressure was less than 100 mm Hg, at 70°C for 6 hours according to A.O.A.C., sections 22.013 and 22.014 (1). Moisture content was calculated from the weight of the dry sample and expressed as percentage of original sample.

Each data point reported is the average for three replicates, and each test was conducted with a fresh sample. All measured values were considered, and the mainframe version of SAS<sup>™</sup> was used to perform the regression analysis.

## RESULTS AND DISCUSSION

Figures 1 to 3 are plots of sorption isotherms for freeze-dried pineapple pulp at different temperatures. Figures 1 and 2 show the adsorption moisture isotherms for freeze-dried pineapple pulp at 5, 25, and 30°C; and 35 and 55°C, respectively. It is possible to observe that the lower the temperature, the higher the moisture content for a given  $a_w$ . This is in agreement with the predictions of equation [4] because  $a_w$  is always between 0 and 1; therefore,  $[-\ln(a_w)]$  will increase whenever  $a_w$  decreases. Similar observations could be made for figure 3, which illustrates the desorption moisture isotherm at 25, 30, 35, and 55°C. This means that freeze-dried pineapple pulp becomes less hygroscopic with an increase of temperature. This is reasonable because the low sugar content of the pulp is one of the few factors able to reverse the observed trend. The temperature effect in equilibrium moisture content is more evident at high water activity levels (0.75 and above). These results agree with those reported by Henderson (6), Lima and Cal-Vidal (9), Roman et al. (12), and DeGois and Cal-Vidal (4) for other fruits dried by several methods. Since freeze-dried products leave a more open structure than other drying methods, it is not self-evident that similar sorption

<sup>4</sup>Trade names in the publication are used only to provide specific information. Mention of a trade name does not constitute a warranty of equipment or materials by the Agricultural Experiment Station of the University of Puerto Rico nor is this mention a statement of preference.

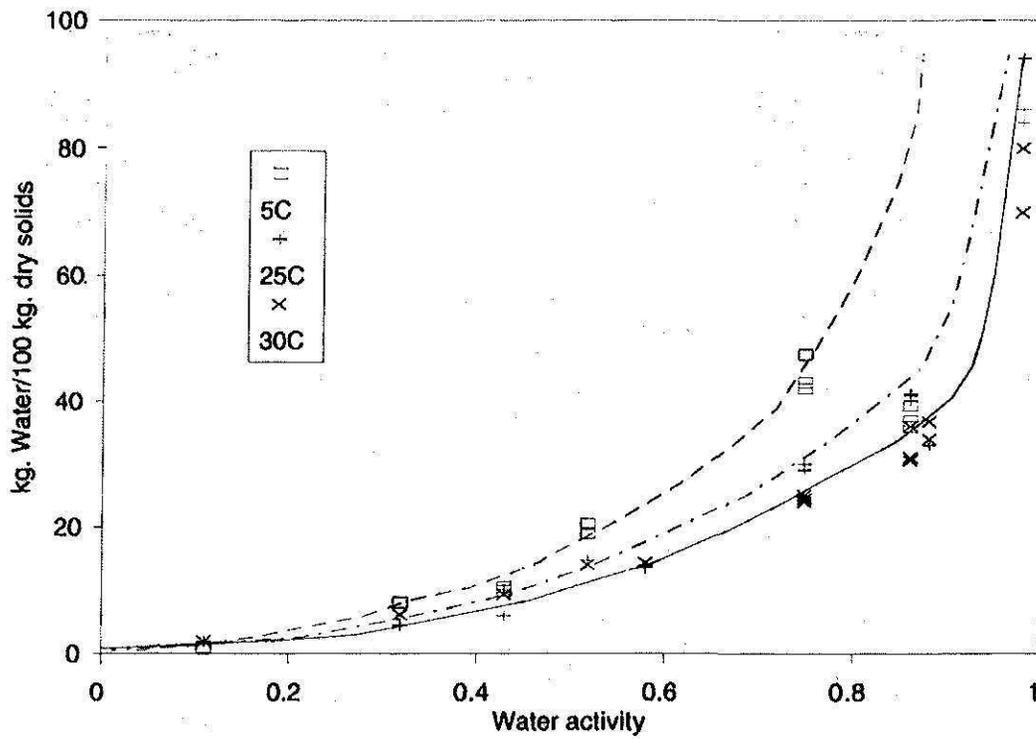


FIG. 1.—Adsorption moisture isotherms for freeze-dried pineapple pulp at 5, 25, and 30°C.

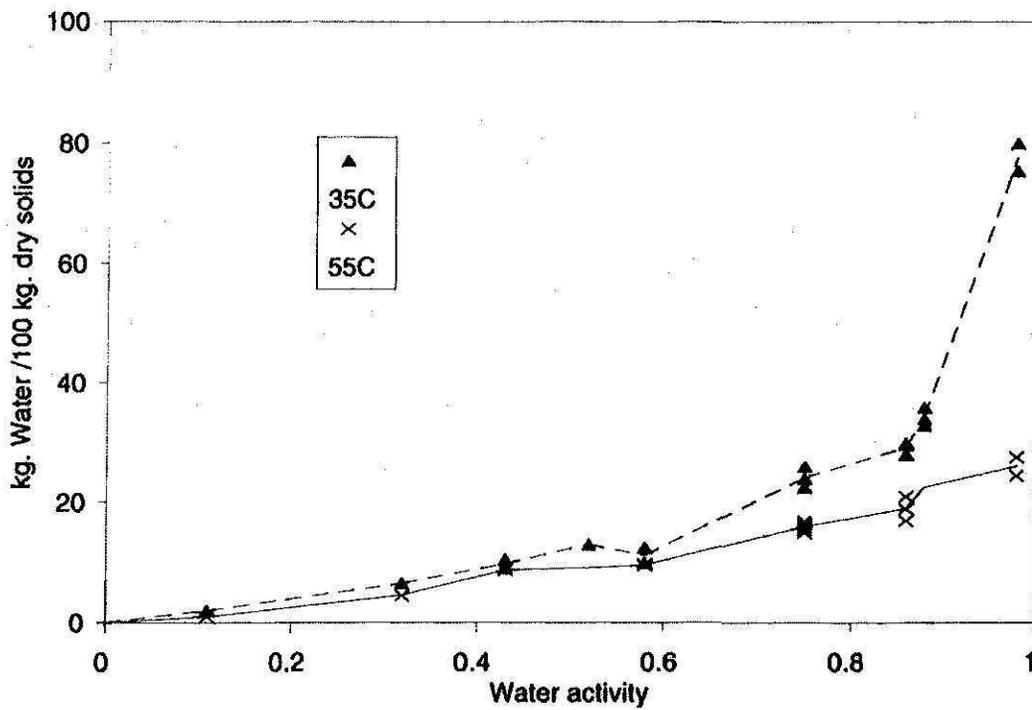


FIG. 2.—Adsorption moisture isotherms for freeze-dried pineapple pulp at 35 and 55°C.

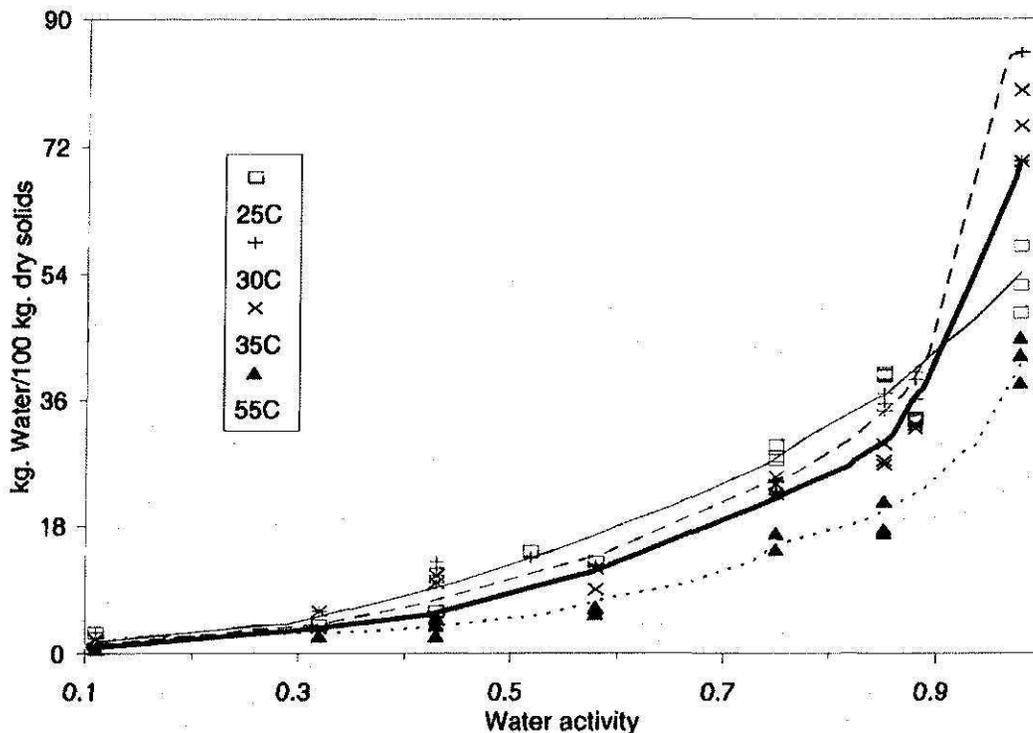


FIG. 3.—Desorption moisture isotherms for freeze-dried pineapple pulp at 25, 30, 35, and 55°C.

patterns will be found. It is relevant to mention that the repeatability for all selected experimental conditions was good, and the maximum dispersion encountered was 3% from the reported mean. One of the reasons for minimal deviations from the mean was the use of a reference material, in this case microcrystalline cellulose, of known sorption properties and without hysteresis.

The heat of sorption was evaluated by equation [1], as indicated in figures 4 and 5, for different moisture contents. The slope of the line,  $Q_s/R$ , decreases as moisture content increases once the monolayer value has been exceeded. This indicates a decrease in the binding energy for water molecules. Tables 1 and 2 show the results obtained for the different moisture levels. It is possible to notice, by comparing heat of sorption values at adsorption and desorption, that for the same moisture content desorption values are lower than adsorption values. Figure 6 shows the relationship between heat of sorption and moisture content. The difference between heat of adsorption and desorption can be attributed to physical or chemical changes in the pineapple pulp surface.

According to adsorption data, the monolayer value is about 20 kg water/100 kg dry solids from adsorption data, which corresponds to the maximum heat of sorption (table 1); desorption data shows the monolayer

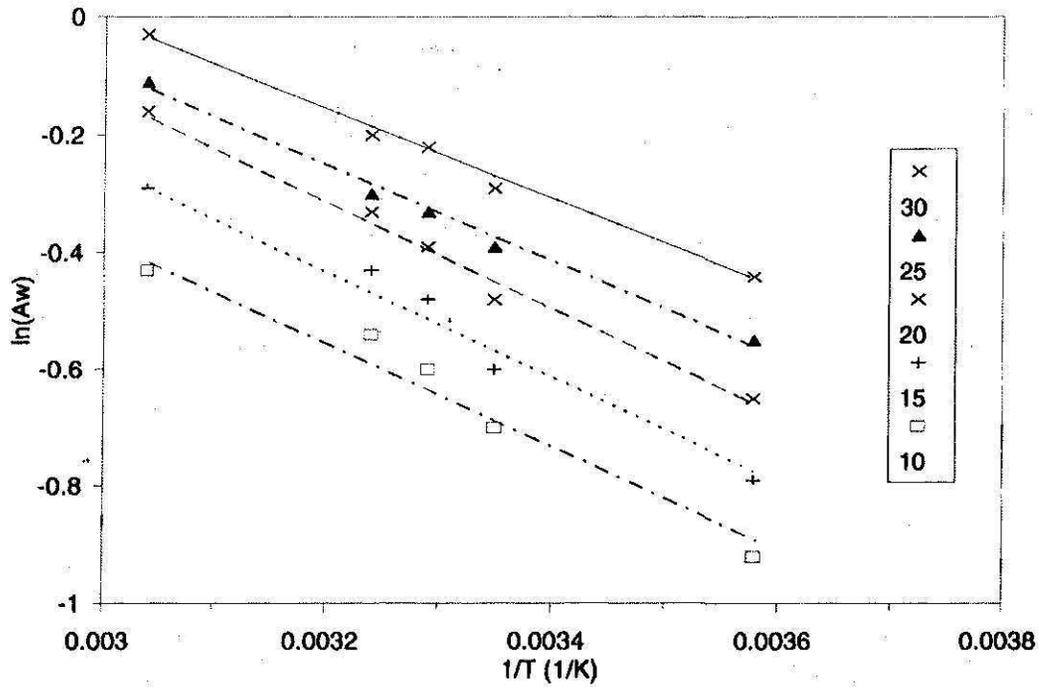


FIG. 4.—Plots of  $\ln(a_w)$  vs the reciprocal of absolute temperature for adsorption data of freeze-dried pineapple pulp at different equilibrium moisture contents.

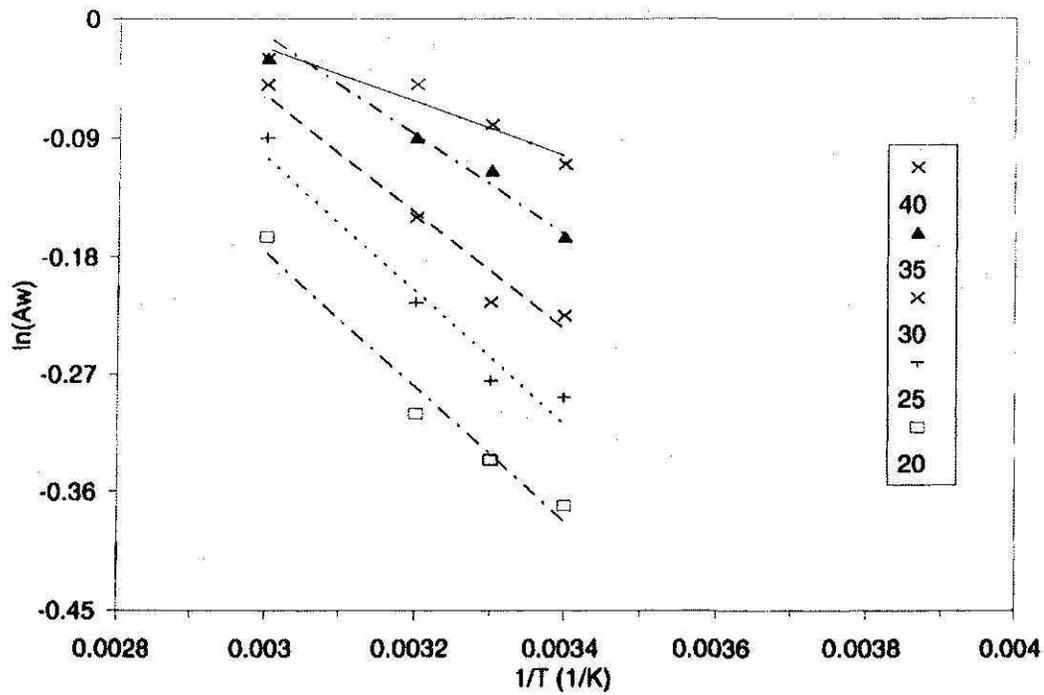


FIG. 5.—Plots of  $\ln(a_w)$  vs the reciprocal of absolute temperature for desorption data of freeze-dried pineapple pulp at different equilibrium moisture contents.

TABLE 1. Heat of adsorption for freeze-dried pineapple pulp.

Moisture content (kg H <sub>2</sub> O/100 kg dry solids)	Q (kJ/mole)	Correlation coefficient
10.0	7.592	0.97
15.0	7.986	0.98
20.0	7.610	0.99
25.0	6.629	0.99
30.0	6.321	0.99

value is about 30 kg water/100 kg dry solids. The difference in monolayer values can be attributed to the hysteresis phenomenon. This phenomenon could be explained by the "ink bottle neck" theory as discussed by Labuza (8). This theory explains hysteresis on the basis of the difference in radii of the porous structure of the sorbent. The latter consists of large-diameter pores simulated by the main body of an ink bottle equipped with narrow passages simulated by the neck of the ink bottle. In adsorption, condensation first takes place in the large diameter cavity. In desorption, the neck of the pore is blocked by a meniscus which can evaporate only when the pressure falls to a certain point where the whole pore empties at once; therefore, for a given amount of water adsorbed, the pressure is greater during adsorption than during desorption. The presence of a persistent hysteresis indicates that the system, although reproducible, is not in true equilibrium, and the process is not reversible. From a practical standpoint, it implies the need to know the prehistory of the sample in order to predict its water activity and related properties.

Figures 7 and 8 are plots of free energy change for freeze-dried pineapple pulp using the adsorption and desorption data. A linear regression analysis was used to determine the slope and intercept values of equation [4]. The results obtained for each temperature are listed in tables 3 and 4. It was found that the slopes of the straight lines for adsorption and desorption data were similar. If this had not been the

TABLE 2. Heat of desorption for freeze-dried pineapple pulp

Moisture content (kg H <sub>2</sub> O/100 kg dry solids)	Q (kJ/mole)	Correlation coefficient
20.0	5.895	0.99
25.0	5.450	0.98
30.0	4.832	0.98
35.0	3.342	0.95
40.0	2.122	0.83

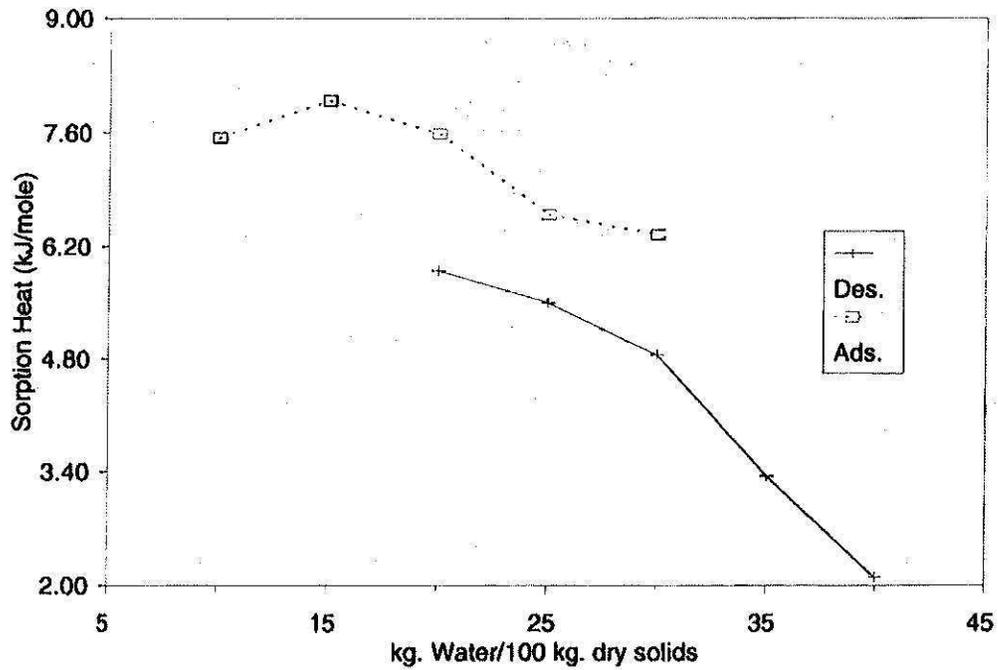


FIG. 6.—Comparison of heats of sorption for freeze-dried pineapple pulp as a function of equilibrium moisture content.

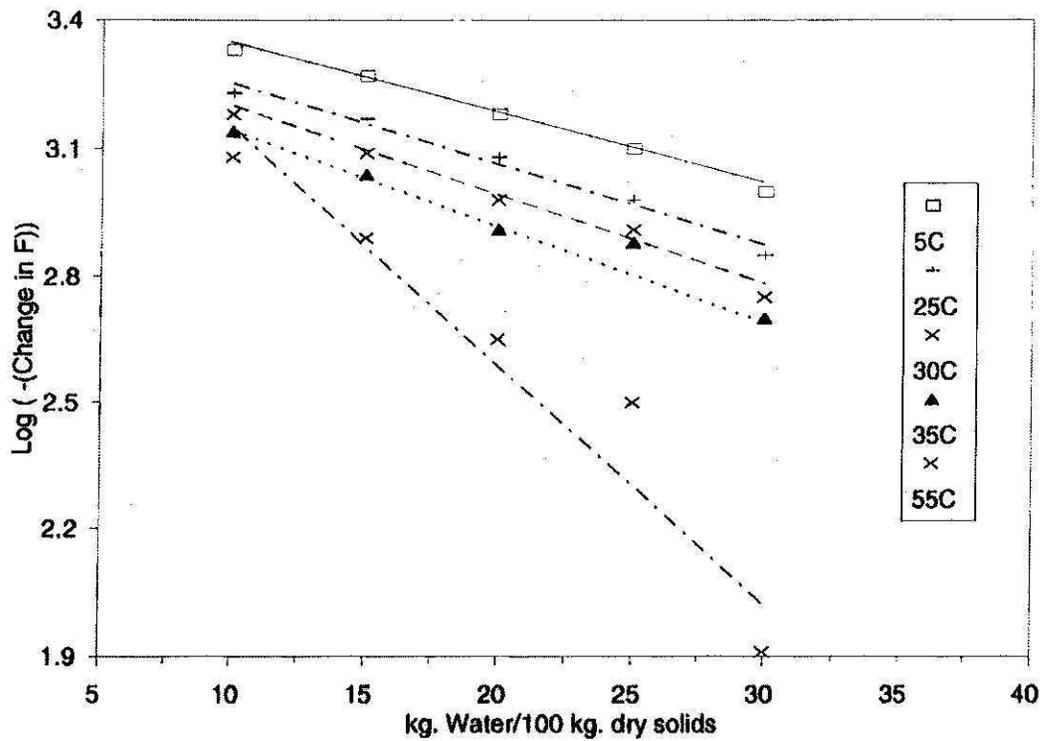


FIG. 7.—Free energy change for adsorption process in freeze-dried pineapple pulp.

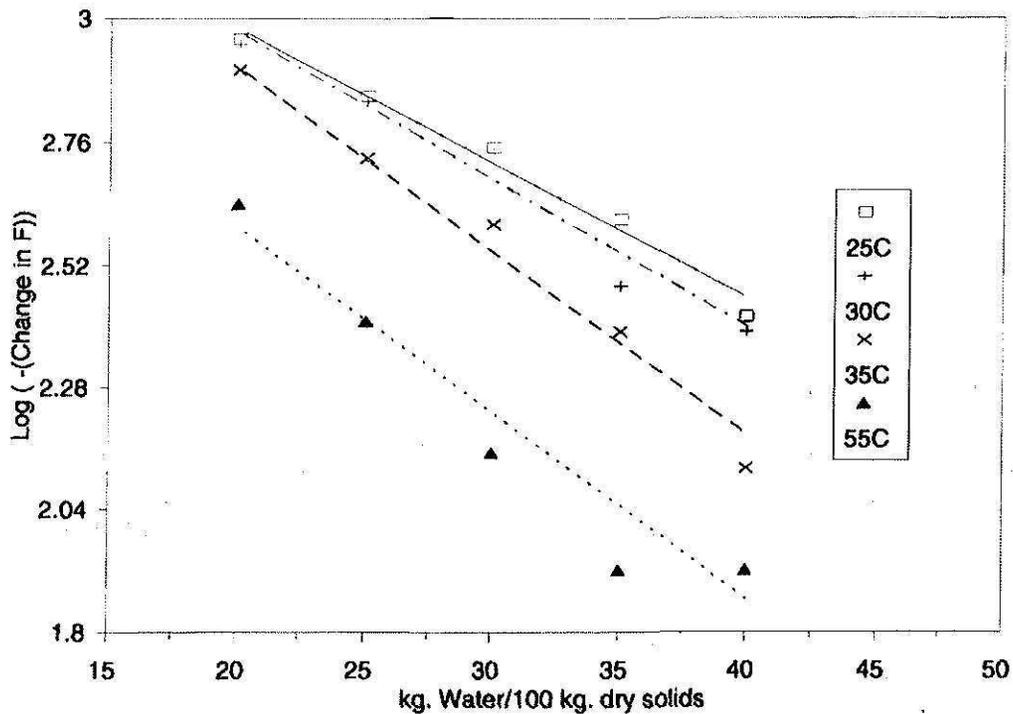


FIG. 8.—Free energy change for desorption process in freeze-dried pineapple pulp.

case, the differences between adsorption and desorption results could be attributed to chemical and physical degradation of the pineapple pulp.

The heat of sorption as a function of equilibrium moisture content for freeze-dried pineapple pulp has behavior similar to that of the reported relationship for other dried whole fruits such as apples (11). The sorption data for freeze dried pineapple pulp obeys the derived equation of the Clausius-Clapeyron relationship (equation[1]). The heat evaluated from adsorption data was found to be higher than from desorption data, and both had the same behavior as a function of moisture content. At the same time, the free energy change could be estimated by equation[4]. The values obtained using this model agreed with those reported by Chung and Pfof (2), Kumar (7), and Rockland and Nishi (11) for other commodities.

TABLE 3. Regression results for free energy change using adsorption data

Temperature (°C)	Slope	Intercept	Correlation coefficient
5	-0.02	3.49	0.99
25	-0.02	3.44	0.99
30	-0.02	3.39	0.98
35	-0.02	3.35	0.97
55	-0.05	3.69	0.94

TABLE 4. Regression results for free energy change using desorption data

Temperature (°C)	Slope	Intercept	Correlation coefficient
25	-0.03	3.52	0.99
30	-0.03	3.59	0.97
35	-0.04	3.67	0.98
55	-0.04	3.38	0.94

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