

**VARIETAL DIFFERENCES IN CHICKPEA FLOUR
(*CICER ARIETINUM*) IN RELATION
TO WATER VAPOR SORPTION**

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ABSTRACT

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Water vapor sorption by four varieties of chickpea flour has been studied at 35°C with the quartz fiber spring technique. The sorption capacity of the flour starch was greater than that of the flour proteins. Values of the diffusion coefficients of water in flours have been calculated. The specific surface areas of the samples have been calculated by the

Brunaur, Emmett, Teller (BET) and Harkins-Jura (HJ) methods. Pore size distribution reveals the presence of micropores in flours. The magnitude of the heat of adsorption and the free energy change for the system rule out the possibility of any chemical interactions involved.

Chickpeas are native to India and are one of the most important pulse crops of the country. From the nutritional point of view, chickpeas have high food value because, compared to wheat and other food grains, they contain a higher amount of protein, fat, calcium, iron, riboflavin, and vitamin C. Chickpea flour is very popular among the rural population. Because it is rich in lysine, arginine, and other amino acids, it is often mixed with wheat flour. Commercial uses of a flour depend almost entirely on its hydration properties. An understanding of the hydration mechanism is essential and it may well be studied from the standpoint of sorption. In the quality characterization of flours, results of such

physicochemical tests as adsorption, loaf volume, and surface area are often used to give an indication of baking potentialities. Sorption studies certainly give an insight into the properties of three-dimensional or conformational structures of proteins and thus help in the assessment of varietal differences.

In spite of the voluminous work that has already accumulated, the unique properties of flour constituents, particularly of the proteins, and their mode of interaction with water are not completely understood. The differences in mixing and baking quality sometimes observed for different flours with similar amounts of protein are puzzling because our knowledge of the hydration mechanism is incomplete.

Few attempts have been made to account for the sorptive behavior of flours on the basis of their physical and chemical characteristics. Little is known about the chemical nature of active sites and there have been relatively few studies of the diffusion of sorbates in these materials.

The purpose of the present investigation is to obtain more information about the interaction of water with flours. The objective is primarily to study the sorption kinetics for the purpose of obtaining diffusion coefficients. Diffusion of a fluid through a solid may be regarded as the movement of adsorbed phase through a solid adsorbing medium. The mechanism is expected to depend on the state of the adsorbed molecules and on the physical and chemical structure of the solid. A systematic study of the flours from different varieties of chickpeas was therefore undertaken.

MATERIALS AND METHODS

Four varieties of chickpeas, namely C-104, C-214, C-235, and G-130 were procured from the pulse breeder, Punjab Agricultural University, Ludhiana. The samples were milled in a laboratory mill and the flour was passed through a 100-mesh British Standard sieve. The following experimental work, all in duplicate, was carried out on the flours.

Determination of Moisture. A known weight of the material taken in a small bottle was repeatedly dried at 100°C to constant weight. Loss in weight represented the moisture content.

Crude Protein. Crude protein was determined by the micro-Kjeldahl method described by McKenzie and Wallace (1), using the conversion factor $N \times 6.25$.

True Protein. Soluble true protein was separated from the nonprotein nitrogenous substances by Stutzer's reagent¹ (2) and the nitrogen was estimated in the precipitates by the micro-Kjeldahl method of AOAC (3).

Ash. Ash was determined by igniting a known weight of the material for 4 hr at 550°C in a muffle furnace.

Separation of Protein and Starch. Flour was defatted by the method of Folch *et al.* (4). Soluble proteins were extracted from 100 g of defatted flour with 2% NaCl (3). The residue was extracted with alcohol to remove any alcohol-soluble proteins. It was finally extracted with alkali (0.1% NaOH) to remove alkali-

¹ Prepared by dissolving 20 g CuSO_4 in 1 liter of water containing 2.5 ml of glycerol. $\text{Cu}(\text{OH})_2$ was precipitated by making the solution slightly alkaline with NaOH. Precipitates were washed with water containing 0.5% glycerol. Then the precipitates were rubbed in a mortar to make a uniform slurry with 10% glycerol, so that 15 ml contained 0.5 g of $\text{Cu}(\text{OH})_2$.

soluble proteins. All these extractions were pooled. Precipitated proteins were centrifuged at 12,000 rpm (0°C). The material was repeatedly shaken with alcohol and finally with solvent ether. The product was dried in open air and used for sorption studies. The remaining material, after removal of the proteins, was dried in air and used as starch.

Water Vapor Sorption. This was carried out on the flours and on the flour proteins and starch by employing McBain-Bakr sorption balances. A detailed description of the technique is given elsewhere (5). The sorption apparatus was kept at 35°C inside an air thermostat of the type built by Vernon (6). A high vacuum pump producing a pressure of 10^{-2} mm Hg was used. The extension of the spring was recorded by use of a cathetometer with a correct reading to 10^{-2} mm.

TABLE I
Description of the Chickpea Flour Samples Used

Sample	Crude Protein ^a %	True Protein ^a %	Moisture %	Ash ^a %
C-104	22.32	20.25	6.25	0.45
C-214	24.16	21.89	7.39	0.39
G-130	25.10	23.15	9.28	1.20
C-235	27.65	25.81	8.42	0.86

^aDry basis.

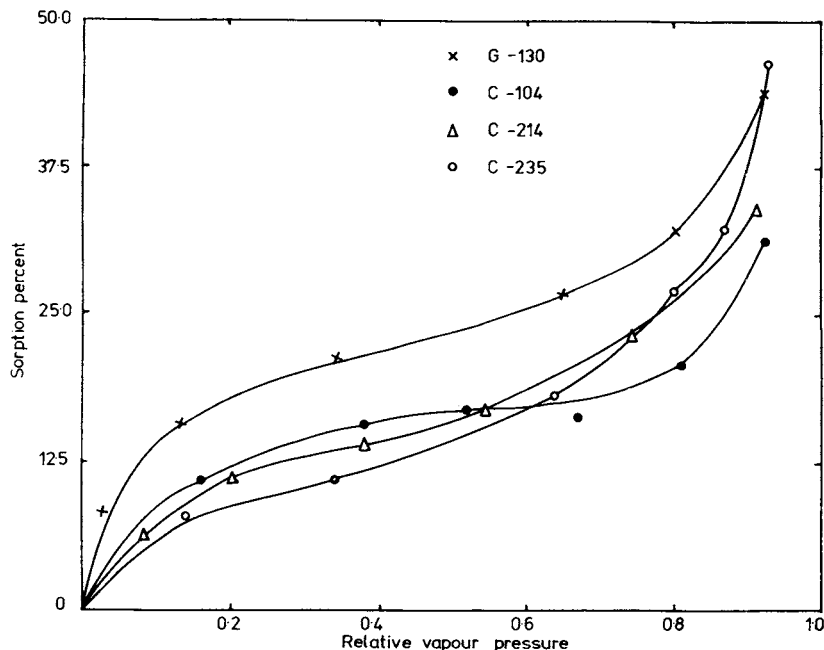


FIG. 1 Sorption isotherms of water with gram flours at 35°C

Fig. 1. Sorption isotherms of water with chickpea flours at 35°C.

RESULTS AND DISCUSSION

Crude and true protein, moisture, and ash of the chickpea flours are given in Table I.

Moisture Sorption by Chickpea Flour. Kinetic studies of the sorption process showed that the rate of sorption of water vapor on flours was quite rapid and equilibrium was established in less than 4 hr. The adsorption was about complete 30 min after the sample was exposed to the vapor. Considerable caking was observed when water was sorbed at high relative pressures at which the degree of adsorption is sufficient to completely and permanently alter the physical nature of the flour and so studies were carried out up to about 0.90 relative vapor pressure. The sorption isotherms are shown in Fig. 1. These curves are similar to those reported by Babbitt (7) and by Sethi and Chopra (8) for the adsorption of water vapor by wheat flour. The amount of water sorbed at about 0.90 relative vapor pressure by C-104, C-214, G-130, and C-235 flour varieties are, respectively, 29.0, 33.5, 43.5, and 46.3 g/100 g of material. These differences reflect real differences in the ability of these materials to bind water. A study and comparison of adsorption isotherms reveal some fascinating results. Variety C-235 has no doubt sorbed its maximum amount of water but the sorption isotherm of G-130 lies above that of C-235 throughout the whole of the pressure range. It may be that G-130 is richer in proteins that have greater affinity to bind water. Another possibility is that this variety contains starch with a lesser degree of inter- and intramolecular cross-linking. The sorption isotherm of C-214 flour also lies above that of C-235 up to about 0.75 relative vapor pressure. Moreover, the isotherms of all the varieties cross each other.

Chickpea flour contains mainly three types of proteins, *viz.* albumins, globulins and glutenins. Albumins constitute a minor fraction of total protein. They are readily soluble in water and salt solutions. They vary significantly among different flours and are of importance as structural modifiers of the complete complex of proteins with water (9). Globulins are simple proteins present in many plant seeds and differ from albumins in being insoluble in water. They are, however, soluble in neutral solutions of the salts of strong acids with strong bases such as NaCl. They interact with water by means of secondary forces such as hydrogen, ionic and apolar bonding. Glutenin proteins have polypeptide chains that are partly folded into compact structures and partly in random conformation. Apart from having intramolecular disulfide bonds that may stabilize the compactly folded part, they also have an average of one

TABLE II
Water Sorption by Chickpea Flours and by
Starch and Protein Separated from the Flours

Sample	Water Taken Up, g/100 g of Dry Material		
	Parent flour	Starch	Protein
C-104	29.0	33.2	31.5
C-214	33.5	33.0	29.7
G-130	43.5	44.0	37.5
C-235	46.3	45.2	31.2

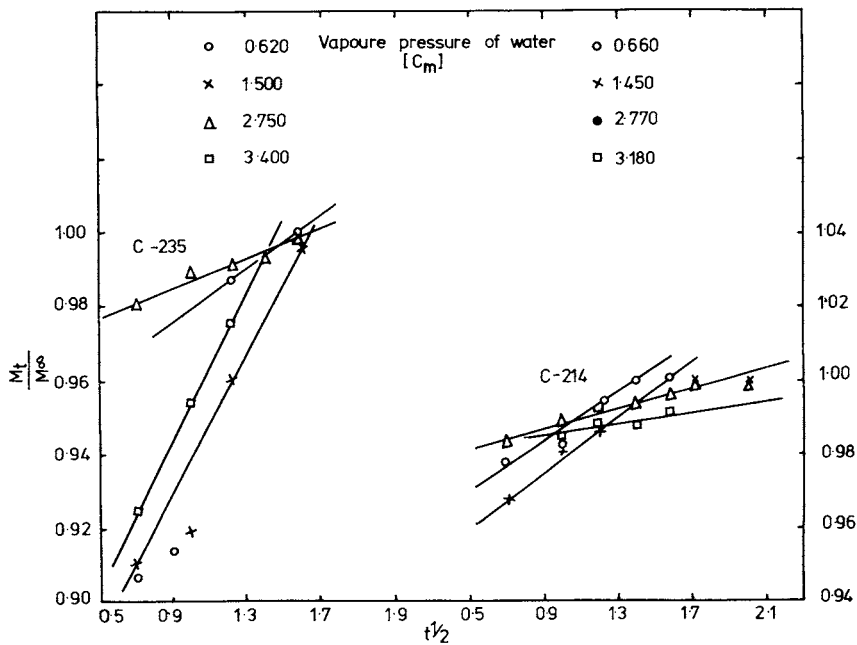
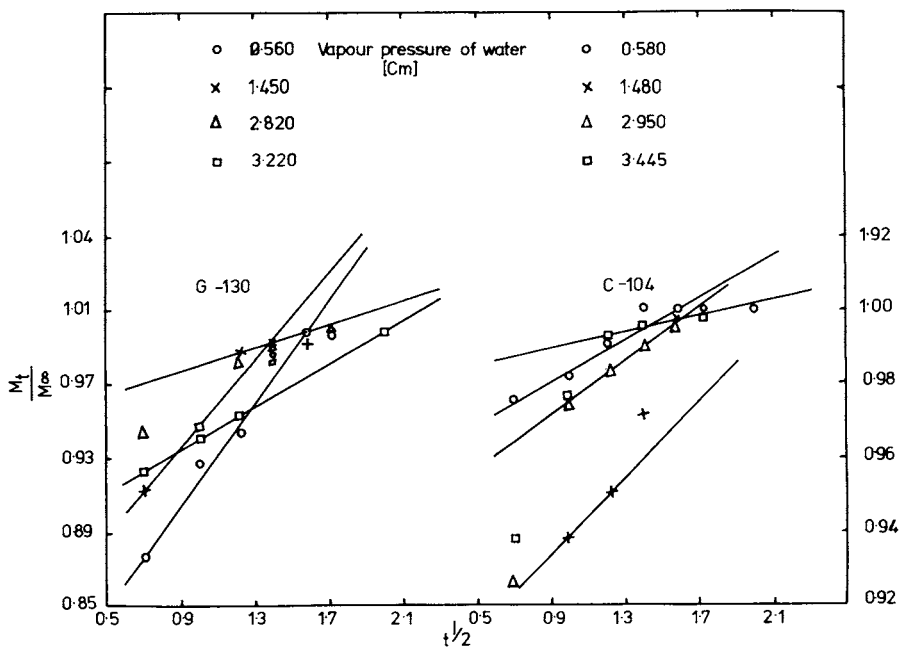


Fig. 2a. Plots of M_t/M_∞ against $t^{1/2}$ for the sorption of water by chickpea flours. b. Plots of M_t/M_∞ against $t^{1/2}$ for the sorption of water by chickpea flours.

intermolecular disulfide bond per molecule that binds glutenin subunits into linear structure. To gain an insight into the differences among chickpea varieties, protein and starch of the parent flours were separated and studied for their sorption capacity with water.

Water Sorption by Flour Protein and Flour Starch. The sorption isotherms of water for protein and starch were similar in shape to those of the parent flour. These are not shown for reasons of space. The experimental results are given in Table II. Differences do exist among starch and proteins from different varieties. An important observation is that the sorption capacity of the starch is higher than that of the flour proteins. The sorption isotherm of the parent flour, as expected, lies between the isotherms of starch and proteins. Another important point is that at low relative pressures (less than 0.30) the parent flour showed higher sorptive capacity than starch or proteins alone. This is in agreement with the theory of active site adsorption.

The above results are in agreement with those obtained by Gur-Arieh *et al.* (10) who observed that the sorption capacity of wheat flour decreased with the increase in protein content. The sorptive power of starch fractionated from wheat flour was higher than that of the gluten fraction. Bushuk and Winkler (11) noted the following trend in water sorption: starch > flour > freeze-dried gluten > spray-dried gluten.

Diffusion Coefficients of Water in Flours. Earlier work on the sorption of water vapor by wheat flours, by Babbitt (7), Bushuk and Winkler (11), Udani *et al.* (12), and in our laboratory (8) has indicated that the rate of adsorption is diffusion-controlled. An attempt has therefore been made in the present work to calculate the diffusion coefficients.

TABLE III
Diffusion Coefficients of Water in Chickpea Flours at 35°C

Variety	Vapor Pressure of Water cm	Average Diffusion Coefficient $\frac{(\bar{D})}{L^2} \times 10^4$
C-104	0.580	669
	1.480	1963
	2.590	919
	3.445	78
C-214	0.660	873
	1.450	1162
	2.770	185
	3.180	71
G-130	0.560	5026
	1.450	2335
	2.820	276
	3.220	743
C-235	0.620	431
	1.500	7857
	2.750	347
	3.400	6773

The rate of sorption of a diluent into a solid is supposed to be controlled by the following two processes: 1) the process in which the diluent vapor is adsorbed into the solid and then dissolved into the surface layer; and 2) diffusion down to the concentration gradient formed inside the solid. The rate of diffusion inside a solid surface is evaluated from the diffusion coefficient. Bucche (13) developed the following equation which is based on the free volume theory:

$$D = A \exp \left(-\beta \frac{V}{V_f} \right) \quad [1]$$

where A and β are constants. The free volume of the system is a function of the temperature and volume of the penetrant. Wilkins and Long (14) obtained the following relation at constant temperature and incorporated the dependence of the free volume of the system on the volume fraction of the penetrant.

$$\log D_T = \log D_{0T} + \alpha_T V_A \quad [2]$$

where α_T is a constant for a given temperature. The average diffusion coefficient is given by:

$$\frac{M_t}{M_\infty} = \frac{4}{L} \cdot \frac{(\bar{D}t)^{1/2}}{\pi} \quad [3]$$

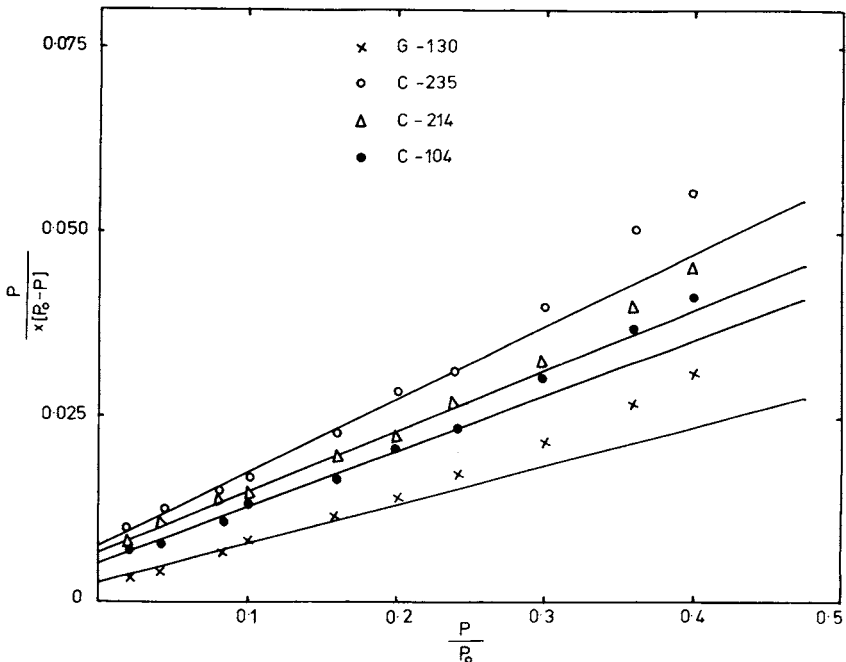


Fig. 3. BET plots of the sorption of water vapor by chickpea flours at 35°C.

where M_t stands for the vapor adsorbed at a time t and M_∞ is the vapor adsorbed at the saturation point. Sorption runs were carried out at four successively increasing vapor pressures of the penetrant. From each sorption run, the mass of the penetrant adsorbed was recorded against time. The quantity M_t/M_∞ was plotted against $t^{1/2}$ at different pressures for different varieties (Fig. 2, a and b). From the slope of each line the diffusion coefficient was calculated. Values of the coefficients at various water vapor concentrations are given in Table III.

From a perusal of the data (Table III), it is evident that there is a marked dependence of the diffusion coefficient on the concentration of the adsorbate. The value of \bar{D} increases first and then declines with the increase in water vapor concentration in C-104 and C-214 varieties. The value, however, continuously decreases with the increase in vapor pressure with G-130 and it shows an irregular trend in the case of C-235 variety. The magnitude of the diffusion coefficient at lower vapor pressure is highest for G-130, followed by C-214, C-104, and C-235.

The dependence on water vapor concentration exhibiting a maximum value of diffusion coefficient is explained by the fact that the first molecules of water are sorbed with the greatest heat of adsorption and therefore they are the least mobile. At low vapor pressures, the water molecules are powerfully bound to

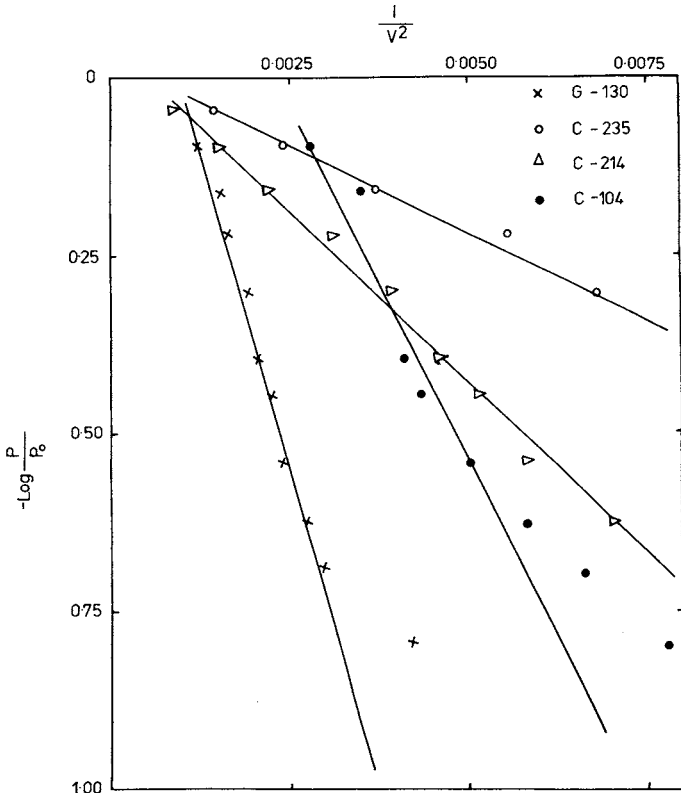


Fig. 4. HJ plots of sorption of water by chickpea flours.

specific sorption sites and the diffusion consists of site-to-site migration of activated molecules. So a sort of two-dimensional mechanism is applicable. However, as the moisture content increases, the primary sites become saturated and the multimolecular formation commences. Now, with the proceeding of the multimolecular sorption, a point is reached where the entering water molecules are held in overlapping force fields. From this point on, a three-dimensional mechanism is applicable. It is evident, therefore, that the transition in mechanism should be accompanied by a rather marked change in diffusion coefficient, which has been verified experimentally.

No specific relation is found to exist between the protein content of the flours and the magnitude of the diffusion coefficient. However, it is worth mentioning that water sorption by cereals and related substances such as proteins, starch, and cellulose is essentially independent of the state of subdivision and is a specific molecular property of the adsorbent itself.

Surface Areas of Flours. All the isotherms in Fig. 1 belong to type II of the well-known classification of adsorption isotherms, indicating formation of multimolecular layers. It was thought of interest to analyze the data first by the Brunaur, Emmett, Teller (BET) equation.

Application of the BET theory. The form of the BET equation most often applied to experimental data (15) is:

$$\frac{p}{x(p_0-p)} = \frac{1}{x_m \cdot c} + \frac{c-1}{x_m \cdot c} \cdot \frac{p}{p_0} \quad [4]$$

According to this, when $p/x(p_0-p)$ is plotted against p/p_0 , a straight line should result. Representative BET plots are shown in Fig. 3. From the slope and intercept, the values of the monolayer capacity (x_m) have been calculated for C-104, C-214, G-130, and C-235 varieties to be 0.1234, 0.1760, 0.1600, and 0.0926 g/g of adsorbent, respectively. From the monolayer capacity, the specific area of the sorbent has been calculated by the equation (15):

$$S = \frac{x_m}{M} \cdot N \cdot A_m \cdot 10^{-20} \quad [5]$$

Taking the cross-sectional area of a water molecule as 10.6 \AA^2 (16), the specific surface areas (S) of the flours C-104, C-214, G-130, and C-235 have been calculated to be 377.1, 416.9, 552.2, and 328.1 m^2/g , respectively.

Bushuk and Winkler (11) observed disagreement between the values of the specific surface area obtained for the flour-water vapor and flour-argon system, in which there is an extensive swelling of the adsorbing material. Chickpea flour also forms a swelling system with water and hence it is interesting to check the values of the specific surface area by application of the Harkins-Jura (HJ) method (17).

Harkins-Jura Method. The HJ equation is:

$$\log \frac{p}{p_0} = B - \frac{C}{V^2} \quad [6]$$

where B and C are constants. The plots of $\log p/p_0$ against $1/V^2$ for various flour

samples are shown in Fig. 4. They are linear up to a considerable range of vapor pressure. These authors suggest the calculation of specific surface area (S) of the adsorbent by the relationship:

$$S = K(A)^{1/2} \quad [7]$$

where A is the slope of the linear plot and K is a constant depending on the nature of the adsorbate. By taking the value of K for water vapor (18) as 3.83, the specific surface areas of the four varieties are calculated to be 541.5 for C-104, 287.7 for C-214, 729.2 for G-130, and 264.2 for C-235.

It is evident that the results of the surface area obtained by the BET method and the HJ equation are not consistent. These differences probably arise because of the different postulates involved. For example, in the BET method one requires knowledge of the molecular size of the adsorbate, whereas in the HJ method this value is not required at all and the value of the constant K is used instead. There is some indication (19) that at least a part of the discrepancy might be due to the swelling that occurs during the sorption of water, although it does not seem likely that the increase in surface area owing to swelling would be extensive enough to account for all these differences.

Pore-Size Distribution. Thomson (Lord Kelvin) (20) discussed in thermodynamic terms the vapor pressure p of a liquid contained in a cylindrical

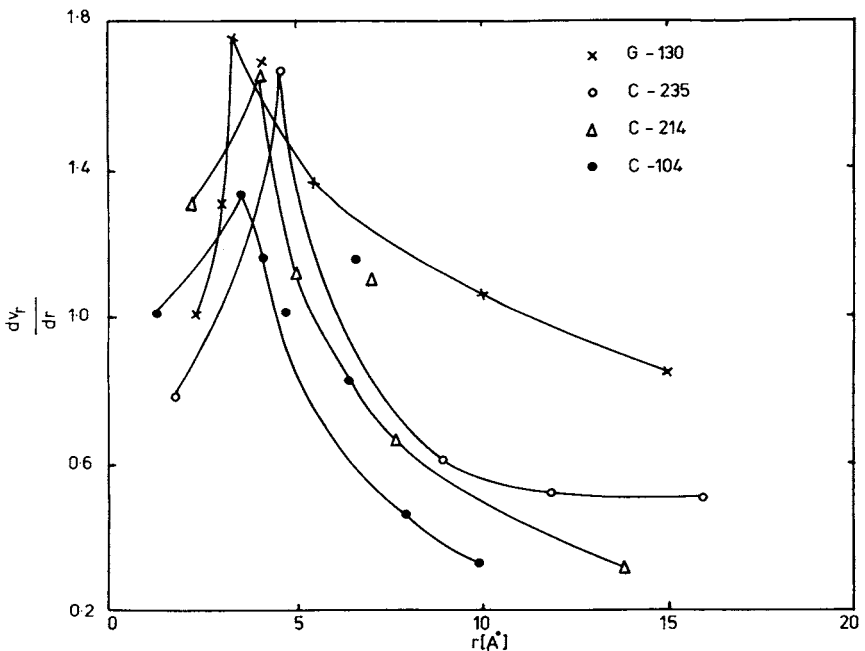


Fig. 5. Pore size distribution of chickpea flours with water at 35°C.

capillary. From his treatment, it is possible to arrive at what is termed the Kelvin equation:

$$\ln \frac{P}{P_0} = - \frac{2V_M \gamma}{rRT} \cdot \cos \phi \quad [8]$$

It is usual to make the simplifying assumption that the angle is zero, *i.e.*, the liquid wets the walls of the pores. From this equation one can calculate the value of r , say r_1 , corresponding to any given point on the isotherm, that is, for any given value of the relative pressure, say P_1/P_0 , and the corresponding value of adsorption, say x_1 . If one were now to neglect the amount adsorbed on the walls, then x_1/ρ would be equal to the volume v_1 of all the pores which have radii up to and including r_1 . According to the capillary condensation hypothesis, all the pores will have become filled when the relative pressure P_1/P_0 has been reached, and ρ is the density of the liquid. One could thus plot a graph of v_r against r and the pore size distribution curve would be the derived curve of dv_r/dr . This was essentially the procedure adopted by Foster (21). The pore size distribution thus

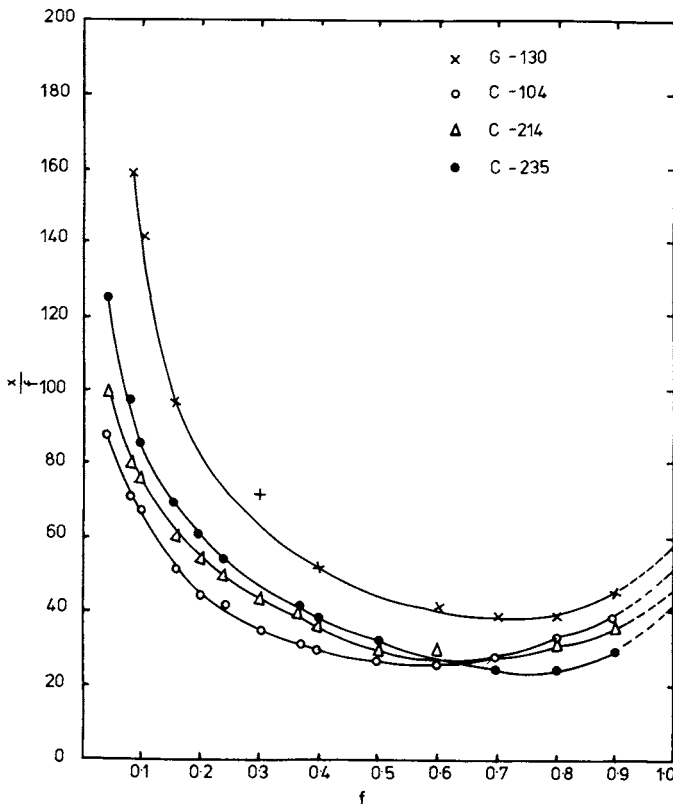


Fig. 6. Plots of x/f against f for the sorption of water by chickpea flours at 35°C.

obtained is shown in Fig. 5. No allowance is made for the changing thickness of the layer adsorbed on the walls of the pores. The values of predominant pore size for C-104, C-214, G-130, and C-235 varieties are 5.5, 6.0, 5.3, and 6.5 Å, respectively. It is concluded that there are micropores in flours, as is suggested by the Dubinin classification of pores (22).

Thermodynamic Quantities. A significant factor for the success of the BET theory is that it provides a means of evaluating the heat of adsorption. The constant c in the BET equation is related to the net heat of adsorption by the following equation:

$$c = e^{(E_f - E_L)/RT} \quad [9]$$

The values of the net heat of adsorption $E_f - E_L$ for the four types of chickpea flours, C-104, C-214, G-130, and C-235, have been calculated to be 773, 1306, 861, and 696 cal/mol, respectively. These values are quite low in magnitude and therefore rule out the possibility of any chemical interaction between the adsorbent and the adsorbate.

The values obtained should only be treated in a qualitative manner. Cassie (23) for example, showed that, in sorption of water vapor by wool which also yields a sigmoid isotherm, the swelling process is highly endothermic and may use as much as 50% of the heat produced by the adsorption process. By analogy, it is suspected that the swelling of the materials used in this study would be endothermic also. So to get a true picture of the magnitude of the heat the values have to be corrected for the heat of swelling; however, that is not possible at this stage because of the nonavailability of a number of physical constants for the flours.

Further, in the isothermal process accompanying the sorption of 1 g of water vapor by the flours, the free energy change, which provides a means of ascertaining the general direction of the vapor sorption under a given set of conditions, has been calculated using the equation:

$$\Delta G = \frac{RT}{M} \int_0^a \frac{P/P_0}{y} \cdot \frac{dy}{y} \quad [10]$$

where 'a' is the weight of the vapor sorbed at relative vapor pressure y and other letters have their usual significance. In order to integrate the above equation, a/y vs. y was plotted (Fig. 6). The area under the curve was multiplied by the quantity RT/M to get the value of the free energy change. The values for C-104, C-214, G-130, and C-235 varieties turn out to be -1.154, -1.288, -1.925, and -1.171 kcal/mol, respectively. This is again indicative of weaker interactions of water with chickpea flour. In fact, it is a case of physical adsorption where only weak molecular forces are involved and the process is a simple condensation one.

Acknowledgment

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LIST OF SYMBOLS AND THEIR MEANING

- A_m = the cross-sectional area of the sorbate.
 D = the intrinsic diffusion coefficient of the diffusion molecules.
 \bar{D} = the average diffusion coefficient.
 E_1 = the heat of adsorption accompanying the sorption of vapor by the solid.
 ΔG = the change in the free energy of the system accompanying sorption.
 L = the film thickness of the adsorbent.
 N = the Avogadro's number.
 P = the vapor pressure of the penetrant.
 S = the surface area of the solid.
 v = the critical hole volume required for the diffusion.
 v_f = the free volume of the system.
 V_A = the volume fraction of the penetrant.
 V_M = the molar volume of the liquid.
 x = the amount of penetrant taken up by the solid at a certain vapor pressure.
 y = the relative vapor pressure of the sorbate.
 γ = the surface tension of the penetrant.

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