Hexane Sorption in Oilseed Meals

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ABSTRACT: Sorptional equilibrium of hexane in oilseed meals was studied as a function of temperature, solvent activity, and oil content. A dynamic technique was implemented based on gravimetric measurements with a Cahn electrobalance. Sorption and desorption isotherms of hexane in sunflower and soybean meals were determined at atmospheric pressure in the range 50 to 95°C. The equilibrium was reached faster during the adsorption process and at high hexane activities. The final equilibrium was not influenced by particle size and sample geometry. Hexane sorption is strongly dependent on temperature, meal composition and oil content, and the effect of hysteresis is negligible. Hexane is mainly retained by adsorption on the cell structure, absorption in the residual oil, and capillary condensation in the meal pores. Experimental equilibrium data were fitted to the GAB equation, and the parameters were determined by nonlinear regression analysis. This model represents satisfactorily the sorption behavior in a wide range of conditions.

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KEY WORDS: Equilibrium, hexane, meals, sorption isotherm, soybean, sunflower.

Most oilseed-crushing industries use solvent extraction with commercial hexane to produce crude oils. Desolventization with water vapor in a desolventizer–toaster is the step of the process that removes the solvent from the oilseed meals. The operation demands significant amounts of steam, electricity, and solvent, and plays an important role in production costs. Additional reasons, such as safety, pollution, potential health risk and regulations, require maximum recovery of solvent. Knowledge of the sorption–desorption equilibrium is needed to evaluate the residual hexane content in the cake as a function of meal characteristics and desolventizing conditions. Sorption isotherms, represented by a suitable correlation, and sorption kinetics are required to model, simulate, and optimize the process.

Several factors could affect the amount of residual hexane in oilseed meals after desolventization. Moisture and hull content of the crushed seed, cooking time, temperature prior to extraction, solvent temperature, and extraction time appear to be the most important (1–4). Residual hexane in canola (1) and rapeseed (2,3) increased significantly with seed moisture content, solvent temperature, and exposure time during extraction.

The sorptional equilibrium in biological systems, such as oilseed meals, is a complex phenomenon because of the heterogeneous structure of the material and the mechanisms of interaction between the solvent and the solid (5,6). The solvent content in the meal can be thought to be due to adsorption on the cellular structure, dissolution in the residual oil, capillary condensation in the microstructure, and vapor retention in solid pores. At lower contents, the solvent is mainly retained by adsorption, which is the result of interactions between solvent and meal components such as cellulose and proteins by hydrogen bonding, while capillary condensation is the prevailing mechanism at higher solvent contents. The equilibrium will depend on meal structure and composition, type of solvent, and temperature.

Complete sorption isotherms of hexane in rapeseed meals at different temperatures have been presented by Roques *et al.* (7,8), who found that the equilibrium is reversible and does not depend on particle size. However, limited information is available on other oilseed meals, and the effect of composition on equilibrium hexane content has not been sufficiently studied.

The objectives of the present work were to determine sorption isotherms of hexane in oilseed meals, particularly focused on sunflower and soybean, by a thermogravimetric method and to investigate the effects of temperature, meal composition, and oil content on the equilibrium.

EXPERIMENTAL PROCEDURES

Samples. Sunflower and soybean meals and sunflower crude oil were obtained from a local crushing plant. The meals were taken from the feed to the industrial desolventizer. The pellets (cylinders of 50–80-mm length and 20-mm diameter) were ground and separated with standard sieves to obtain a more homogeneous material. Fractions between 0.3 and 2.4 mm, with a mean particle size of 1.1 mm, represented about 87% of the total weight and were used in these experiments. The meal oil content was 1.8 and 1.95% for sunflower and soybean, respectively. The hull content in sunflower meal, determined by density differences, was approximately 10%, and the oil content of the hull fraction was 0.97%. A sample free of oil was obtained by Soxhlet extraction with hexane in three

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stages for 24 h. Samples with different oil contents were obtained by reimpregnating the meal with oil–hexane mixtures and desolventizing.

Before each run, the meal was dried in a vacuum oven at 70°C for 12 h. A sample of approximately 1 g weight was placed in a cylindrical pan and dried in the electrobalance at 105°C with a dry nitrogen stream for at least 3 h until a constant weight was observed. This sample was assumed to be practically free of solvents. Then, the temperature was lowered to the working conditions.

Experimental method. A dynamic technique based on gravimetric measurements with a Cahn Electrobalance Model 1000 (Cahn Microbalances, Boston, MA) was implemented to study both equilibrium and kinetics of sorption–desorption of solvents in solids (9–12). A simplified schematic diagram of the experimental apparatus is shown in Figure 1. The measurement of weight changes in the range of micrograms is hampered by buoyancy, radiometric effects, thermomolecular effects, gas flow effects, free gas convection, electrostatic effects, aerodynamic forces, and zero drift (11,12). Some of these problems are considerably reduced with the symmetric design adopted in this work (9). Jacketed Pyrex tubes (790-mm length, 16-mm i.d.) were connected to both Electrobalance sides. To decrease electrostatic charges, the sides of the tubes were wetted with a liquid antistatic solution provided by Cahn. The tubes were heated with a glycerol thermostatic bath (Model TU-16A; Techne Inc., Princeton, NJ). The temperature of the sorption chamber was measured with a platinum thermocouple that was placed 2 mm below the sample pan. The temperature control system maintains the chamber temperature within a range of ± 0.1°C of the desired value.

A nitrogen gas stream (99.95% purity) was saturated with *n*-hexane [Merck (Darmstadt, Germany), 99% purity] by passing through a 600-mL jacketed Pyrex tube (500 mm length, 40 mm i.d.) and a condenser (Model 80T; Polyscience, Niles, IL). The temperature in the tube, maintained with a thermostatic bath (Model Paratherm III; Julabo Inc., Kutztown, PA), was slightly higher than the temperature in the condenser. This saturated nitrogen stream is combined with two dry nitrogen streams to adjust the composition of hexane; one of them is used to prevent the solvent from entering the balance weighing unit. All connecting tubing (1/4-in. o.d.) was covered with heat tape to keep the system warm and prevent hexane condensation. The flow rates were measured by volumetric flow meters (Model Gilmont F1100; Cole-Parmer Instrument Co., Niles, IL). All temperature probes (chromel-alumel; Omega Engineering Inc., Stanford, CT) were connected to a digital thermometer (Model 2190A; Fluke Corp., Everett, WA). The total gas flow and its hexane content were checked by passing the stream leaving the balance through a buret–condenser connected to a refrigerated circulator at −15°C (Model 1268-02; Cole-Parmer) and a bubble flowmeter.

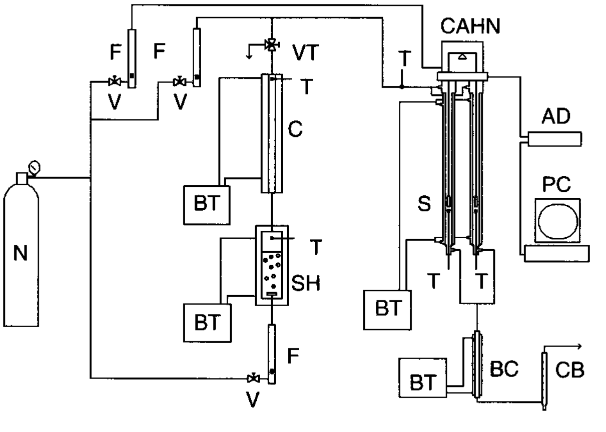

FIG. 1. Dynamic sorption apparatus for isotherm measurements. AD, data acquisition system; BC, buret–condenser; BT, thermostat; C, condenser; CB, bubble flowmeter; F, flow-rate meter; N, nitrogen; PC, personal computer; SH, hexane saturator; T, thermocouples; V, valve; VT, three-way valve.

By adjusting the flow rates and controlling the saturator–condenser temperatures, the adsorption chamber was kept at a specified hexane activity. The balance output was connected to a data acquisition system (Adalab-PC; Interactive Microware Inc., State College, PA), and the weight change of the sample was continuously measured at predetermined time intervals (from 6 to 40 s). After equilibrium was achieved, the activity was changed to the next specified value. Typical runs at 65°C for sunflower and soybean meals are depicted in Figure 2.

Additional studies not shown in this work indicated that particle size, sample geometry, and amount of meal have a strong influence on sorption kinetics but do not affect the final equilibrium.

Hexane activity. The criterion for phase equilibrium in a multicomponent, multiphase system can be stated by equality of chemical potential or fugacity. Thus, the chemical potential of a given species, in this case hexane, must be the same in all phases in which it is present at equilibrium. On this basis, the following general expression can be obtained for solvent equilibrium between liquid–vapor or solid–vapor phases (13):

$$a_h = \frac{\phi_h^v y_h P}{\phi_h^{\text{sat}} P_h^{\text{sat}}} \qquad [1]$$

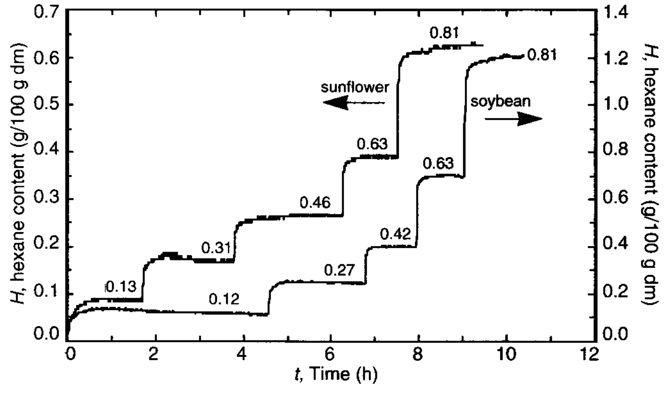

FIG. 2. Typical run of hexane sorption in sunflower and soybean meals at 65°C.

TABLE 1
Fugacity Coefficients of Pure Hexane (ϕ_h^{sat}) and of Hexane in a Gas Mixture with Nitrogen (ϕ_h^v)

Fugacity coefficient	Mol fraction of hexane	Temperature 50°C	65°C	80°C	95°C
ϕ_h^{sat}	—	0.9700	0.9577	0.9432	0.9264
ϕ_h^v	0.10	0.9811	0.9839	0.9862	0.9881
	0.20	0.9733	0.9773	0.9805	0.9832
	0.40	0.9606	0.9664	0.9711	0.9750
	0.60	0.9516	0.9584	0.9645	0.9693
	0.80	0.9463	0.9541	0.9606	0.9658
	0.90	0.9449	0.9530	0.9596	0.9650

Here, a_h represents the hexane activity, y_h the molar fraction of hexane in the gas phase, P the total pressure, and P_h^{sat} the saturation pressure. Fugacity coefficients of hexane at saturation, ϕ_h^{sat}, and in the gas mixture, ϕ_h^v, can be calculated from virial equations as a function of temperature, pressure, and composition (13,14). Predicted values of fugacity coefficients are presented in Table 1. A usual practice in sorption experiments is to simplify the above equation to $a_i = y_i\ P/P_i^{sat}$. However, the effect of fugacity coefficients should be considered in hexane sorption.

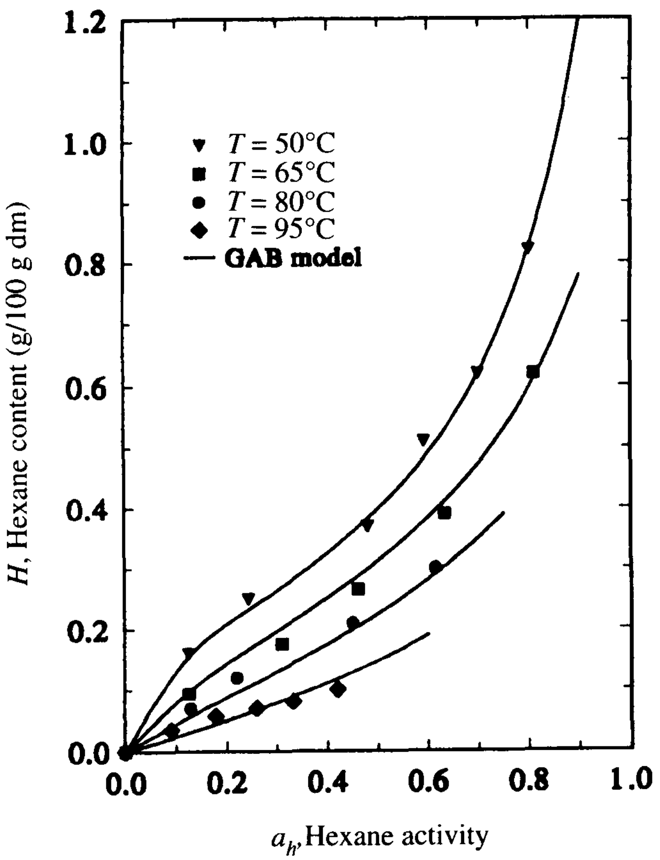

FIG. 3. Hexane sorption isotherms in sunflower meals. Experimental data are fitted with the GAB model.

RESULTS AND DISCUSSION

Experimental sorption isotherms at different temperatures for sunflower and soybean meals are shown in Figures 3 and 4. Experimental limitations due to the low boiling point of the solvent did not allow us to obtain hexane activities higher than 0.4–0.5 at high temperatures. Hexane contents increase drastically with hexane activity and decrease with equilibrium temperature. The isotherms resemble the sigmoid shape that is characteristic of water sorption, indicating a change in the phenomenon from multimolecular adsorption to capillary condensation.

The temperature dependence approximately follows a Clausius–Clapeyron relationship, which can be used to evaluate the net heat of sorption (5,6). At high hexane contents, the net heat of sorption is low compared to the heat of vaporization, less than 5 kJ/mol against 26.5–29.5 kJ/mol, and the total heat of sorption approaches the heat of vaporization, indicating that the solvent behaves almost like free hexane. The heat of sorption increases as the hexane content decreases, more rapidly in the region of small contents. For low coverage, 0.1 g/100 g, it rises up to 37 kJ/mol and 22 kJ/mol for sunflower and soybean meals, respectively. The equivalent value for rapeseed meals was 36 kJ/mol (7).

Comparison of isotherms for sunflower and soybean, together with those for rapeseed (7,8) at two similar temperatures, are given in Figure 5. It shows that rapeseed and soybean meals retain more hexane than sunflower meals under the same conditions. Sunflower and soybean meals have approximately the same oil content; thus the differences should be attributed to the solids composition and structure. Unfortunately, the oil content in rapeseed meal was not specified. Anyway, the results are in agreement with the pilot-plant experiments reported by Wolff (2) in which the residual hexane in rapeseed meals was significantly higher than in soybean and sunflower meals. According to Grant *et al.* (1), the hexane content in canola meal increased with the protein content. It can be concluded that hexane sorption is determined by the amount and type of proteins, which provide more active sites for solvent adsorption in soybean and rapeseed meals. Higher contents of cellulosic material, as for sunflower meal, result in a lower hexane content but give the strongest bonds because of the higher desorption energies as stated above.

Several equations have been proposed to represent sorptional equilibria in foodstuffs, particularly for water sorption. The Guggenheim–Anderson–De Boer (GAB) model has been widely used because of its theoretical background, its mathematical flexibility to represent experimental data, and its applicability for engineering calculations (15). When applied to hexane sorption, the GAB equation can be expressed as:

$$H = \frac{H_m C K a_h}{(1 - K a_h)(1 - K a_h + C K a_h)} \qquad [2]$$

In the above equation, H is the hexane content on a dry basis (g of hexane per 100 g of meal free of solvent), a_h is the hexane activity, and H_m is the hexane content on a dry basis

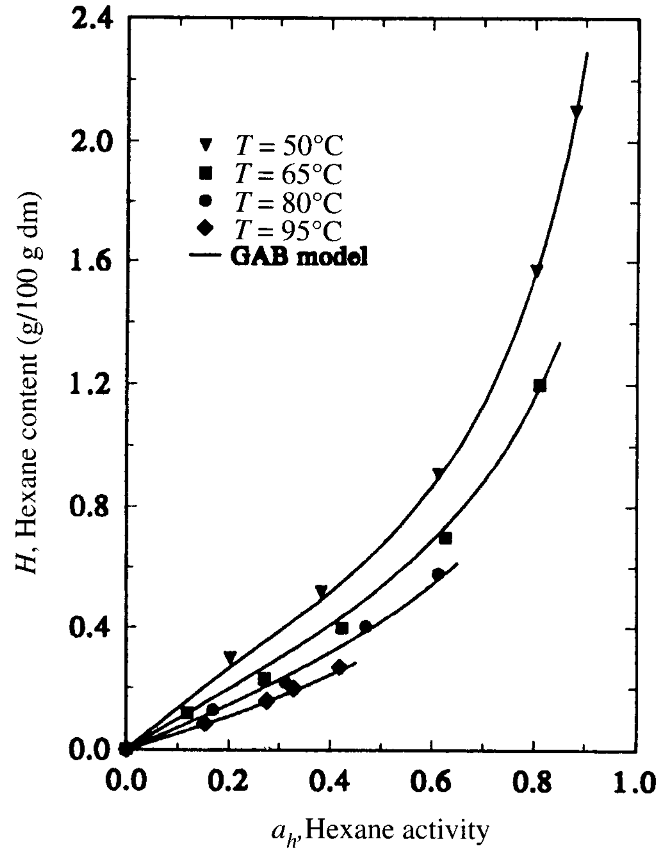

FIG. 4. Hexane sorption isotherms in soybean meals. Experimental data are fitted with the GAB model.

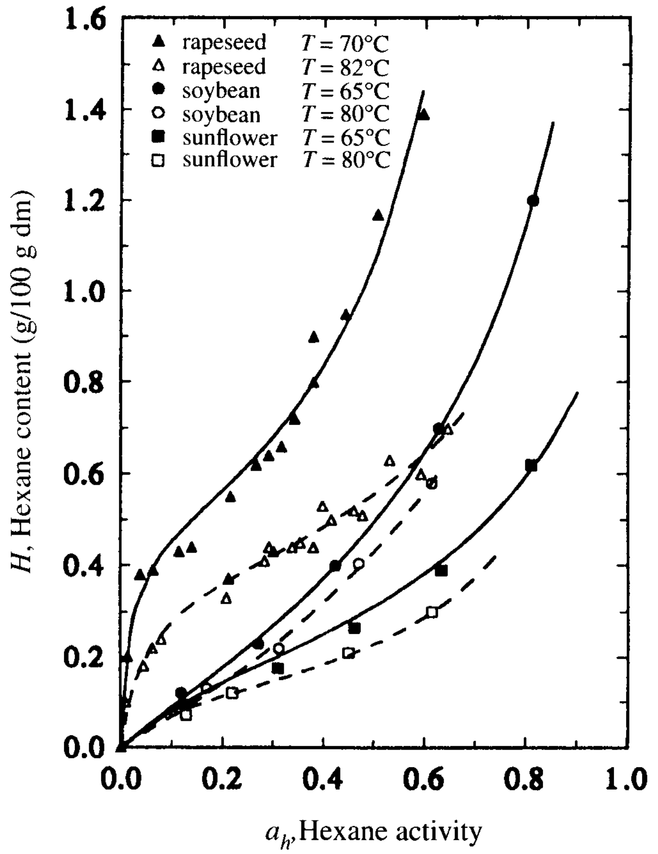

FIG. 5. Comparison of hexane sorption in sunflower and soybean meals (this work) and reapeseed meal (Refs. 7,8) at different temperatures.

at saturation of the active adsorption sites (monolayer). C and K are sorption constants that are related to the energies of interaction of sorbed molecules and the absolute temperature T as follows:

$$C = C_o \exp\left(\Delta H_C / RT\right) \quad [3]$$

$$K = K_o \exp\left(\Delta H_K / RT\right) \quad [4]$$

where ΔH_C and ΔH_K represent the differences between the molar sorption enthalpies of the monolayer and the multilayer and between the multilayer and the pure solvent, respectively, and R is the ideal gas constant.

The experimental isotherms of hexane in sunflower and soybean meals of this work and those of rapeseed meal (7,8) were fitted to the GAB equation by using nonlinear regression analysis (16). The resulting GAB parameters are given in Table 2. Note that calculated monolayer contents for soybean and rapeseed were twice the value for sunflower, in accordance with the previous discussion. Model predictions are compared with experimental data in Figures 3 to 5. They show that the GAB equation adequately represents the sorptional behavior of hexane on meals in a wide range of solvent activities and temperatures.

Grant *et al.* (1) found that canola meals had higher residual hexane contents than canola hulls, while Wolff (2) and Evrard and Guillaumin (3) reported an opposite effect in rapeseed meals. According to Grant *et al.* (1) and Wolff (2), residual oil content in the meal is not an essential parameter in the retention of residual hexane, at least in a limited range of oil contents. Hexane sorption at 50°C by the main components of sunflower meals is shown in Figure 6. It shows that hexane adsorption in the hulls is slightly lower than in the meals, indicating that elimination of hulls would increase the hexane content in sunflower meals. However, this effect would be low because of the range of hull contents usually found in the industry. On the other hand, the hexane content at equilibrium in crude sunflower oil was two orders of magnitude higher than in the meal. The presence of oil increases the hexane content in both the meal and the hull fraction.

The influence of the oil content on hexane sorption was studied in detail, and the results for sunflower meals are pre-

TABLE 2
Parameters of the GAB Equation for Adsorption of Hexane in Sunflower, Soybean, and Rapeseed Meals[a]

Parameter	Sunflower	Soybean	Rapeseed
C_o [–]	1.930×10^{-6}	3.117×10^{-3}	3.010×10^{-13}
K_o [–]	5.280×10^{-2}	9.172×10^{-2}	1.201×10^{-7}
H_m [g/100 g dm]	2.503×10^{-1}	5.183×10^{-1}	5.670×10^{-1}
$\Delta H_C/R$ [K]	4.986×10^{3}	2.262×10^{3}	1.114×10^{4}
$\Delta H_K/R$ [K]	9.109×10^{2}	7.296×10^{2}	5.373×10^{3}

[a] GAB, Guggenheim–Anderson–DeBoer.

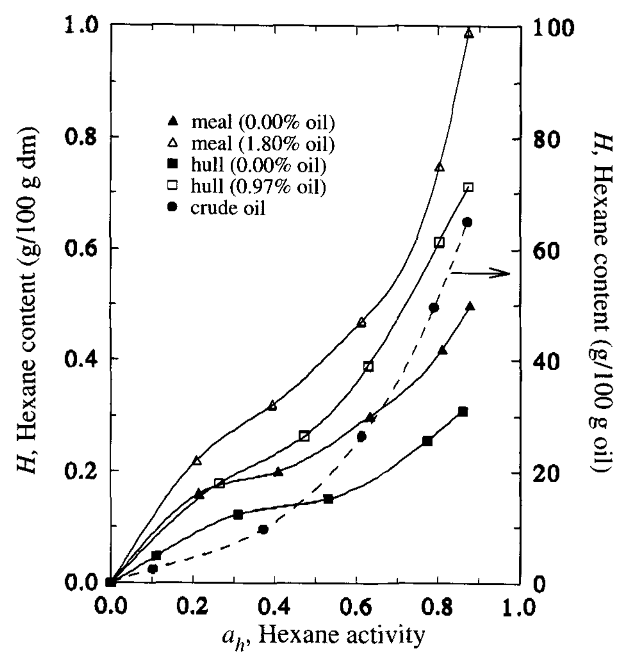

FIG. 6. Hexane sorption in sunflower meal components at 50°C.

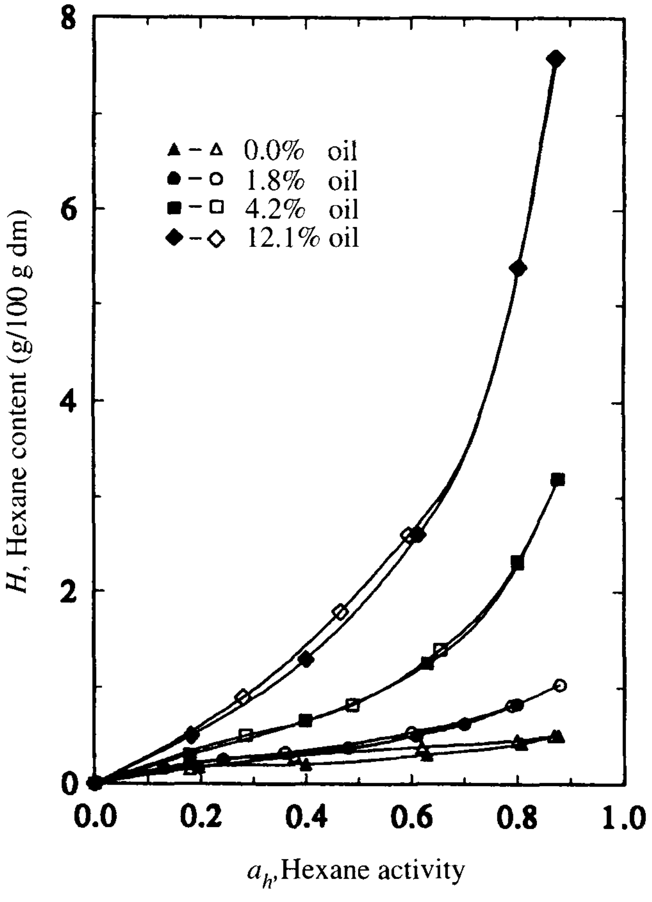

FIG. 7. Hexane sorption in sunflower meals at 50°C showing the effect of oil content and hysteresis. Filled and empty symbols represent adsorption and desorption phenomena, respectively.

sented in Figure 7. A noticeable effect of the oil content on the equilibrium is observed, indicating that a significant amount of the solvent is retained by absorption or dilution in the oil fraction. This effect can be predicted by using thermodynamic vapor–liquid equilibrium data for hexane–oil mixtures.

Differences between sorption and desorption isotherms were also investigated, and the results at 50°C are shown in Figure 7. The phenomenon is related to adsorption on the active sites and nonreversible changes in the structure, and does not depend on the oil content. It can be concluded that the effects of hysteresis on hexane sorption are small and can be neglected for engineering calculations.

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