

Water–Hexane Sorption in Sunflower Meals

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ABSTRACT: Sorption equilibria of water and hexane in sunflower meals were determined at atmospheric pressure and temperatures from 50 to 95°C. Adsorption–desorption experiments, for both individual vapors and water–hexane mixtures, were carried out using a dynamic technique based on gravimetric measurements with a Cahn electrobalance. The isotherms were fitted to the Guggenheim–Anderson–deBoer sorption equation, and the heat of sorption was evaluated from experimental results. In the range of temperatures investigated, water sorption was several times higher than hexane sorption, the differences increasing with solvent activity. The net heat of sorption that resulted was significantly higher for hexane than for water. Water sorption isotherms were slightly affected by temperature, especially at water activities greater than 0.6. Some hysteresis was observed in water sorption at 50°C, but it was practically negligible at higher temperatures. Hexane previously adsorbed in the meal did not affect significantly the sorption of water. On the contrary, water previously adsorbed in the meal increased the amount of adsorbed hexane.

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

Solvent extraction with commercial hexane is used by most seed-crushing industries to produce oil from oilseeds. After the extraction, the meal is treated with live steam in a unit known as desolventizer-toaster (DT) to remove the solvent retained within the solid particles. Inside the DT, the meal moves down, releasing its solvent content to a vapor phase that moves up in countercurrent flow. As a result of this procedure, solid particles are put in contact with a water–hexane vapor mixture of changing composition along their path through the unit.

Knowledge of sorption equilibria as a function of meal properties and process conditions is required to model the desolventizing process and to predict the residual hexane in the meal after this step. Because of the heterogeneous structure of biological materials and the mechanisms of interaction between vapors and solid, such equilibrium in oilseed meals is a complex phenomenon depending on meal structure and composition, type of solvent, solvent activity, and temperature (1–3). Previous experimental works on desolventization

of canola (4,5), rapeseed (6), and soybean flakes (7) have found a strong dependence of residual solvent on seed moisture content, supporting the idea that hexane sorption is affected by the water adsorbed on meals.

Even though much work has been done on adsorption–desorption equilibria of water in different biological materials, in particular oilseeds and their byproducts (8–16), limited information is available at relatively high temperatures. On the other hand, adsorption of solvents other than hexane has not received the same attention (3). Finally, studies on adsorption of vapor mixtures in food materials are rather scarce (17,18), and no information has been found for the water–hexane system.

The objective of this work was to investigate the interaction of water and hexane during their sorption in sunflower meals. Adsorption/desorption isotherms of these solvents and their mixtures were determined at different temperatures by using a thermogravimetric method (3). The equilibrium results were modeled by a suitable sorption expression, the Guggenheim–Anderson–deBoer (GAB) model, and the energy involved in the sorption process was evaluated as the net isosteric heat of sorption.

EXPERIMENTAL PROCEDURES

Samples. Sunflower meal was obtained from the feed to an industrial desolventizer in a local crushing plant. Samples were prepared as described in a previous work (3). After grinding and separating with standard sieves, fractions between 0.3 and 2.4 mm (with a mean particle size of 1.1 mm) were selected in order to obtain a more homogeneous material. The meal oil and hull contents were 1.8 and 10%, respectively. Before each adsorption experiment, samples were dried in a vacuum oven at 70°C for 12 h.

Experimental setup. Sorption isotherms were determined by means of an experimental unit developed to work with adsorption–desorption of either individual vapors or binary vapor mixtures in solids. The technique, based on gravimetric measurements with a Cahn Electrobalance Model 1000 (Cahn Microbalances, Boston, MA), has been described in detail elsewhere (3). A second saturation vessel was added to work with binary vapor mixtures. In this case, two nitrogen streams saturated in different solvents were combined to produce a single stream, and diluted with an extra stream of pure nitrogen. Vapor activities in the mixture were estimated according to mixing rules (19) and

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adjusted by controlling the flow rates and the saturator–condenser temperatures. A cryogenic bath was used to condense the vapor mixture at the end of the solvent circuit, after leaving the measurement unit, in order to check the resulting vapor activities. After equilibrium was achieved, the activity was changed to the next specified value. A typical run of water sorption in sunflower meal at 65°C is depicted in Figure 1 (case A).

The effect of one solvent on the sorption of the second solvent in sunflower meal was determined at constant temperature. The sample was exposed to one solvent until sorption equilibrium was reached. Then, the vapor composition was changed, allowing the other solvent to be adsorbed simultaneously on the solid, while keeping constant the first solvent activity. The results were compared to those obtained by individual and simultaneous solvent sorption.

Typical experiences of sorption of hexane–water mixtures on sunflower meal at 65°C are also shown in Figure 1. In the first case (B), a meal sample was initially exposed to a nitrogen stream carrying hexane vapor at a given activity ($a_h = 0.43$) until hexane equilibrium was reached ($W_h = 0.268$ g hexane/100 g dry matter). Then, a second nitrogen stream saturated with water vapor was added to the mixture, and the flow rates were controlled to obtain a given water activity ($a_w = 0.20$) while hexane activity remained constant ($a_h = 0.43$). Once the new equilibrium was reached, hexane was desorbed by eliminating this solvent in the nitrogen stream. This yielded a third equilibrium corresponding to water sorption. In the second case (C), simultaneous adsorption of a hexane–water mixture ($a_h = 0.43$ and $a_w = 0.20$) was carried out. When binary equilibrium was reached, hexane vapor was removed, keeping a_w constant.

RESULTS AND DISCUSSION

Water sorption. Water adsorption isotherms for sunflower meal at different temperatures (50 to 95°C) are presented in

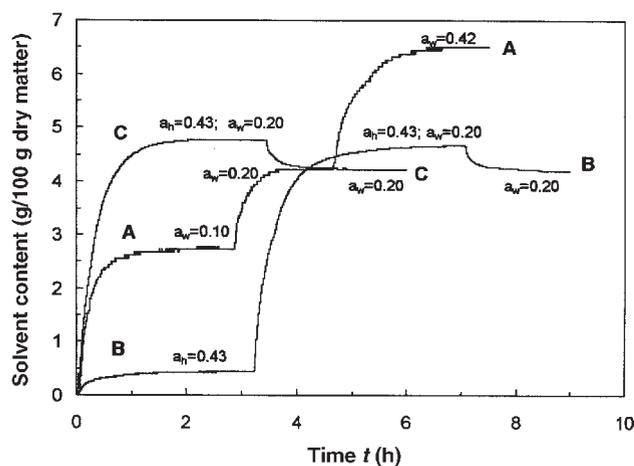


FIG. 1. Typical curves of sorption in sunflower meal at 65°C. (A) Water vapor; (B) hexane and water separately; (C) water and hexane simultaneously. a_h , hexane activity; a_w , water activity.

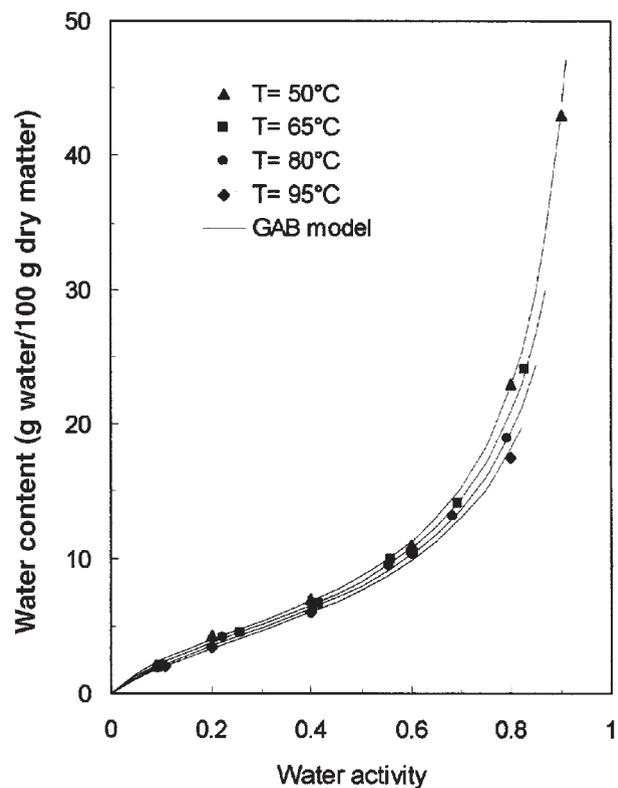


FIG. 2. Water sorption isotherms in sunflower meals. Experimental data were fitted with the Guggenheim-Anderson-deBoer (GAB) model.

Figure 2. The isotherms exhibit a sigmoid shape typical of most food products, the water content decreasing slightly with equilibrium temperature. The isotherms can be divided into three regions (1,9): a low a_w (<0.2) or monolayer region, where water is held by high hydrophilic bonding on polar sites in the solid; an intermediate multilayer adsorption region, where water is retained more weakly by hydrogen bonds inside of pores and in the fiber structure; and a high a_w (>0.5–0.6) region, in which most condensed water is mechanically retained inside void spaces where it has many properties of liquid water.

The temperature effect on water sorption in the range investigated was less important than in other fruit and vegetable products (1,9). Little differences in moisture content were observed at water activities lower than 0.6, but differences increased at higher relative humidities (Fig. 2).

The results at 50°C are compared with other data for sunflower products reported in the literature (expressed on an oil-free basis) in Figure 3. It has been found that hygroscopic equilibrium in sunflower seeds is not influenced by oil content, which is inactive for moisture sorption (12,14). Sunflower products show relatively few differences in water sorption among varieties when expressed on an oil-free basis; what differences there are can be attributed to their different carbohydrate and protein contents (11–13). It has been reported that sunflower hull adsorbed more water than sunflower endosperm, the seed showing an intermediate behavior (14). However, Figure 3 suggests that water-binding ca-

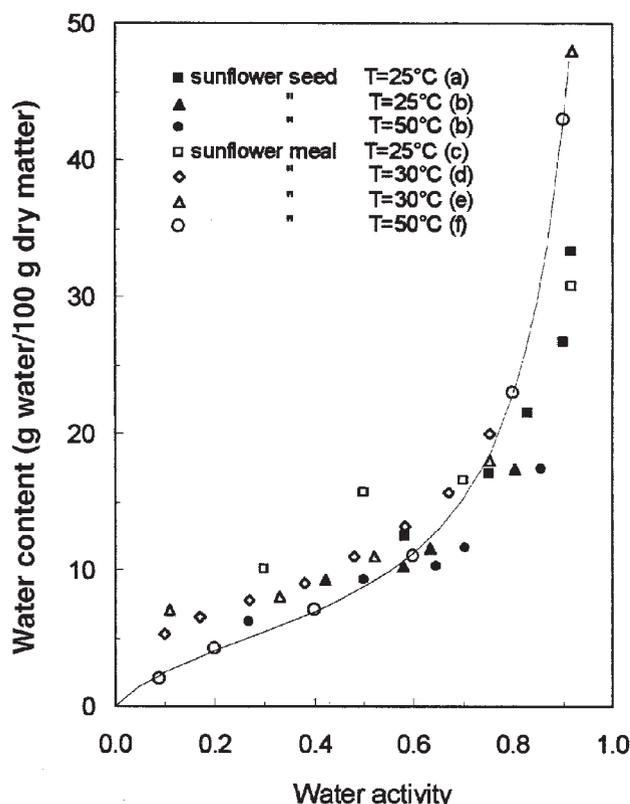


FIG. 3. Water sorption isotherms in sunflower seeds and meals. (a) Pollio *et al.* (12); (b) Rovedo *et al.* (14); (c) Huffman *et al.* (11); (d) Mok and Hettiarachy (10); (e) Kilara *et al.* (13); (f) this work.

capacity of sunflower meals is slightly higher than that of sunflower seed, probably owing to structural changes during the preparation and extraction processes, in accordance with previous studies (10).

Sorption equilibrium of sunflower meals was modeled by the GAB equation. The GAB equation has been widely used to represent water sorption in foods because of its theoretical foundations and mathematical flexibility as well as its applicability in engineering calculations (8,9). It can be expressed as:

$$W = \frac{W_m C k a_w}{(1 - k a_w)(1 - k a_w + C k a_w)} \quad [1]$$

where W is the water content of a solid (dry basis), W_m is the water content of the monolayer, and a_w is the water activity. The temperature dependence is included in the sorption constants C and k as follows:

$$C = C_o \exp(\Delta H_c/RT) \quad [2]$$

$$k = k_o \exp(\Delta H_k/RT) \quad [3]$$

where ΔH_c and ΔH_k represent the differences between the molar sorption enthalpies of monolayer and multilayer and between multilayer and pure solvent, respectively, T is the temperature, and R the ideal gas constant.

Experimental data were fitted to the GAB equation by using a quasi-Newton-type algorithm for nonlinear regression analysis (20). Model fitting is shown in Figure 2, and the resulting GAB constants are presented in Table 1 as they compare with those for other oilseeds and meals. It can be seen that the GAB equation adequately describes water sorption in sunflower meals in the whole range of temperatures and a_w investigated.

Monolayer values predicted for sunflower meal are similar to those reported for sunflower seed, using either the Brunauer-Emmett-Teller model (14) or the GAB model (9). It has been observed in several food products that monolayer water content decreases with temperature. Apparently, the effect is not important in oilseed meals in which monolayer values remain practically constant with temperature (Table 1). Some uncertainty in monolayer values can be due to the few available experimental data in the low a_w region. It can be seen that canola meal (15) and, to a lesser extent, soybean meal (16) show a higher water-binding capacity than sunflower meal. A similar behavior was observed for hexane sorption, which can be attributed to the solid composition and structure (3). It can be concluded that monolayer values for oilseed meals are in the range of 5–9 g water/100 g dry matter, and are notably affected by the type of seed but not by temperature.

Temperature functionality of water sorption in sunflower meals was modeled by replacing into Equation 1 the expressions for C and k given by Equations 2 and 3 and by fitting all data to the resulting equation by nonlinear regression. The resulting GAB constants are shown in Table 2 and compared with those obtained for hexane sorption (3).

Heat of sorption and hysteresis. The energy requirement involved in sorption phenomena is known as the isosteric heat of sorption (Q_{st}). The following expression based on the Clausius-Clapeyron relationship has been widely used to predict the net heat of sorption (Q_s), defined as the difference between the above and the heat of vaporization of pure solvent (ΔH_v):

$$\left\{ \frac{\partial \ln a_w}{\partial (1/T)} \right\}_s = \frac{-(Q_{st} - \Delta H_v)}{R} = -\frac{Q_s}{R} \quad [4]$$

Heat of sorption was evaluated from the slope of $\ln a_w$ vs. $1/T$ for different solvent contents, for both water and hexane sorption. The net heat for water sorption decreased from 4.5 kJ/mol near the monolayer (5.0 g water/100 g dry matter) to 1.5 kJ/mol near the condensation zone (40.0 g water/100 g dry matter). On the other hand, the net heat for hexane sorption (3) ranged from 29 kJ/mol at very low solvent content (0.2 g hexane/100 g dry matter) to 7 kJ/mol at high hexane contents (0.7 g hexane/100 g dry matter). The compared values for heat of vaporization of pure water and hexane are 39.9–40.7 and 26.5–29.5 kJ/mol, respectively. At high solvent contents Q_s tends to zero for both solvents but especially for water, indicating that most sorbed molecules behave practi-

TABLE 1
GAB Constants for Water Sorption in Oilseeds and Meals^a

Product	T (°C)	GAB constants			Reference
		W_m	C_W	k_W	
Sunflower meal	50	5.014	7.263	0.983	This work
	65	4.921	6.426	0.969	
	80	5.097	5.988	0.944	
	95	5.724	4.333	0.882	
Sunflower seed	25	5.11	16.803	0.835	9
Sunflower seed	23	2.22	28.4	0.919	8
Ground sunflower seed	10	3.748	19.590	0.763	10
	20	3.508	19.086	0.786	
	30	3.254	20.420	0.822	
Rapeseed	25	3.55	10.627	0.876	9
Canola meal	16	9.06	61	0.66	15
	22	9.25	41	0.63	
	34	9.60	25	0.59	
Soybean seed	25	5.11	30.739	0.959	9
	25	6.02	18.388	0.927	
Soybean meal	30	6.970	3.424	0.890	16

^aGAB, Guggenheim-Anderson-deBoer equation; W_m , water content of the monolayer; C_W and k_W , sorption constants.

cally as pure liquid. As the solvent content decreases, the heat of sorption increases more drastically for hexane than for water. This behavior indicates that energy requirements to remove sorbed solvent from solid are significantly higher for hexane than for water in the range of temperatures investigated. Note that these results are in agreement with the predictions of the GAB model (Table 2), where the enthalpy differences between monolayer and multilayer (ΔH_c) and multilayer and pure solvent (ΔH_k) were approximately 5.4 and 7.8 times higher, for hexane sorption than for water sorption.

The results obtained for water sorption can be compared with those reported for sunflower seed (14) and other meals (21). In the first case, Q_s values were about 10 and 1.7 kJ/mol at low and high humidity contents, respectively (5 and 15 g water/100 g dry matter in oil-free basis). These values are higher than the net heat of sorption for sunflower meals, probably due to the more organized structure of the seed. Sorption experiments with wheat and defatted soybean meal (16) gave Q_s values of 8.87 and 7.65 kJ/mol, respectively, in the monolayer zone, slightly higher than for sunflower meals.

Figure 4 shows water adsorption and desorption cycles in sunflower meal at two temperatures. Some hysteresis was ob-

served in water sorption at 50°C, but the differences were very small at higher temperatures. A similar behavior was observed in hexane sorption studies (3). Several theories to explain water vapor sorption hysteresis in foods have been published, most of them based on either the alteration of solid structure or cap-

TABLE 2
GAB Constants for Water and Hexane Adsorption in Sunflower Meal^a

Parameter	Water	Hexane ^b
W_m, H_m (g/100 g dry matter) ^a	5.071	0.2503
C_o (-)	4.010×10^{-1}	1.930×10^{-6}
k_o (-)	5.970×10^{-1}	5.280×10^{-2}
$\Delta H_c/R$ (deg. K)	9.299×10^2	4.986×10^3
$\Delta H_k/R$ (deg. K)	1.161×10^2	9.109×10^2

^aMonolayer value for water (W_m) and hexane (H_m) adsorption. $C_o + k_o$, entropic accommodation factors; ΔH_c , difference between molar sorption enthalpy of monolayer and multilayer; ΔH_k , difference between molar sorption enthalpy of multilayer and pure solvent. For other abbreviations see Table 1.

^bFrom Reference 3.

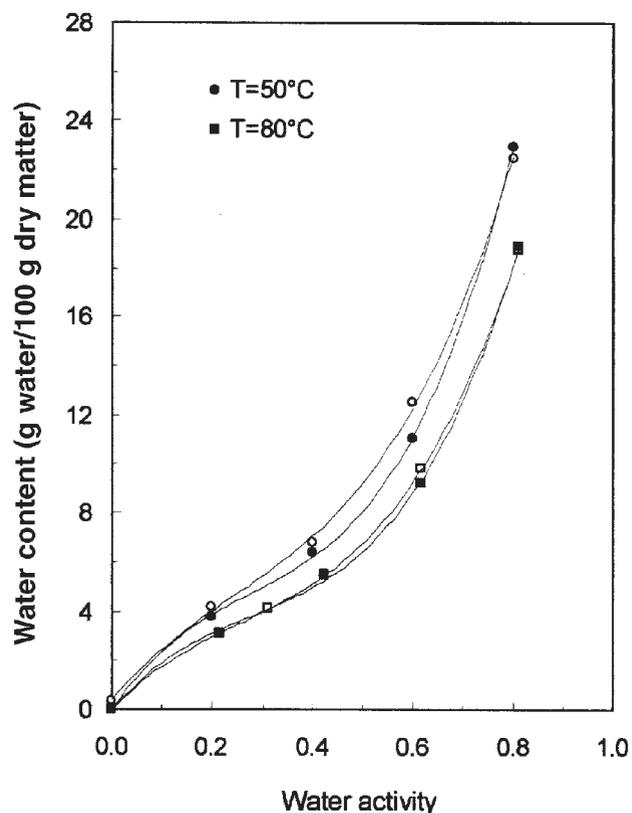


FIG. 4. Water sorption isotherms at two temperatures. Closed and open symbols represent adsorption and desorption phenomena, respectively.

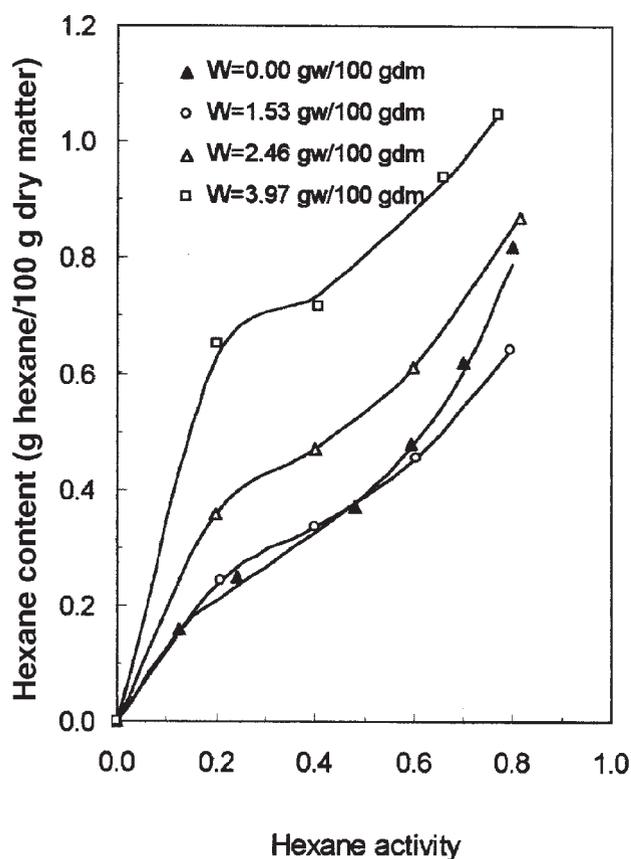


FIG. 5. Effect of water content on hexane sorption in sunflower meal at 50°C. Abbreviations: gw, grams of water; gdm, grams of dry matter; W, water content.

illary concepts. In our case, the influence of nonreversible changes in the structure should be very low because the meal samples were fully dried before the experiments. It can be concluded that hysteresis effect on water and hexane sorption in sunflower meal can be neglected for engineering purposes.

Water-hexane sorption. Sorption of water on sunflower meal was more than one order of magnitude higher than hexane sorption. At the monolayer value, the amount of water was approximately 20 times higher than the amount of hexane, the differences increasing up to near 50 times in the region of high solvent activities. This behavior makes it too difficult to analyze the interaction between both solvents. Water and hexane molecules have little in common, the first being relatively smaller and polar, with more affinity for polar groups that conform active sites. The size of molecules is not enough to explain its capacity to adsorb on solids, and variables such as heat of sorption can establish different behavior between solvents (2). In the case of hexane-meal equilibrium, solvent content in meal can be explained as the adsorption in cellular structure, dissolution in residual oil, capillary condensation in microstructure, and vapor retention in solid pores (2,3). At lower contents, the solvent is mainly retained by adsorption, while capillary condensation and dissolution are the prevailing mechanisms at higher solvent contents.

It can be observed in Figure 1 that final water equilibrium after either previous (B) or simultaneous (C) hexane sorption was practically the same as that reached in water sorption experiments (A) at the same water activity ($a_w = 0.20$). A similar behavior was found at other water and hexane activities. No appreciable change in meal structure was observed after hexane sorption, at least at this very low oil content and in the range of hexane activity studied. On the other hand, according to monolayer values, the amount of active sites used for hexane adsorption is relatively low as it compares with water adsorption. It can be concluded that hexane does not alter the meal structure significantly and that water does not compete with hexane for sorption sites. Thus, hexane content in sunflower meals has a negligible effect on water sorption.

Experiments for determining the influence of water in hexane sorption were carried out in the same way as described above, but the order of solvent adsorption was changed. Resulting isotherms at 50°C are summarized in Figure 5. It can be observed that the effect of water on hexane sorption is important, in accordance with desolventization pilot plant experiences for rapeseed meal (5,6). Unfortunately, only the initial water content has been specified in these studies.

One could propose that this behavior is mainly due to the effect of water on solid structure, since its presence caused some swelling, as was noted in water sorption experiment. During simultaneous adsorption of water and ethanol in starch (17,18) it was observed that water is adsorbed first, producing a light solid swelling, and then ethanol is adsorbed with a negligible change in the solid structure. For this system, no noticeable differences were found between the adsorption of single solvents and the mixture. In our case, a higher water content in the meal increased hexane retention. Adsorbed water in meal may influence the retention mechanism of hexane by enhancing the availability of active sites for a second solvent sorption, enhancing capillary condensation due to changes in porosity and effective pore size, and increasing solvent accessibility into residual oil.

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