Two-Phase Solvent Extraction of Canola

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ABSTRACT: The equilibrium relationships in the extraction process that was developed in our research laboratory for the treatment of canola were studied. In the process, hexane is used as well as CH_3OH that contains 5% (vol/vol) H_2O and 0.08% (w/w) NaOH to simultaneously produce improved meal and high-quality oil. Equilibrium data for canola oil in the hexane–CH_3OH/H_2O/NaOH, meal–hexane, and meal–CH_3OH/H_2O/NaOH–hexane systems are reported. A high partition coefficient for oil between hexane and the polar phase provided a large driving force for mass transfer. The presence of the CH_3OH phase improved oil extraction, probably by rupturing the cell structure. The process proved to be a somewhat less desirable replacement for $CH_3OH/H_2O/NH_3$ extraction and recovered 93.5% of the oil and 91.8% of the protein in the seed, while with $CH_3OH/H_2O/NH_3$, the oil and protein recoveries were 96.8 and 94.0%, respectively. The NaOH treatment removed only 50.2% of the glucosinolates, and some of the oil was hydrolyzed by the NaOH, making the process less effective, despite its simplicity.

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KEY WORDS: Canola meal, canola oil, canola seed, extraction, glucosinolates, oil equilibrium.

Conventional processing of rapeseed involves mechanical pressing and solvent extraction to separate the oil and meal. Our laboratory developed a novel two-phase solvent extraction system for the treatment of canola to produce an improved meal and to simultaneously extract a high-quality oil. (1,2). The process uses 10% (w/w) NH_3 in 95/5% (vol/vol) CH_3OH/H_2O as a polar phase and hexane as a nonpolar phase. A recent modification of the process involves the use of 0.08% (w/w) NaOH, as a replacement for NH_3, in CH_3OH/H_2O (3). With the aim of providing a better understanding of the mechanism of oil extraction with NaOH in our process, equilibrium experiments in two- and three-phase systems were carried out. Equilibrium data are invaluable in determining extraction efficiencies and designing continuous extraction columns. Then, NH_3 and NaOH in our two-phase solvent extraction process were compared in terms of their overall effectiveness. The oil, meal and gum (solids dissolved in the methanol phase) mass distribution, oil and protein recoveries, and glucosinolate removal were determined.

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The polar solvent has several functions in this system: it dissolves most polar compounds, including low-molecular-weight carbohydrates, nonprotein nitrogen, hydratable phospholipids, soaps and glucosinolates, and it inactivates enzymes, in particular myrosinase (1). The dissolved solids in the polar phase represent about 10% of the seed solids.

MATERIALS AND METHODS

Materials. Canola seed (mixture of Global, Delta, and Triton cultivars) was obtained through the courtesy of CanAmera Foods (Hamilton, Ontario, Canada). The chemical composition was determined to be: 46.4 ± 0.2% oil (dry basis); 22.8 ± 0.8% protein (dry basis); and 8.43 ± 0.65 µmol glucosinolates per gram of air-dried, oil-free meal. Technical-grade methanol and hexane were obtained from Canada Colors and Chemicals Ltd. (Toronto, Ontario, Canada). Anhydrous ammonia and 50% (w/w) NaOH (aq) were obtained from Canadian Liquid Air Ltd. (Montreal, Quebec, Canada) and BDH Inc. (Toronto, Ontario, Canada), respectively. All chemicals used for analytical work were of reagent grade and obtained from major chemical suppliers.

The $CH_3OH/H_2O/NH_3$ solution was prepared by bubbling anhydrous ammonia through methanol that contained 5% (vol/vol) water at 0°C. The quantity of dissolved ammonia was determined by titration with 0.1 N H_2SO_4. The solution was made up to the required ammonia content (10% w/w) by dilution with ammonia-free solvent. The CH_3OH/NaOH/H_2O solution was prepared by adding 50% (w/w) NaOH (aq) to 95/5% (vol/vol) methanol/water to make a 0.08% (w/w) NaOH solution.

Analytical methods. The moisture content was determined gravimetrically (4). The oil content was determined by Soxhlet extraction with hexane (5). The crude protein content (as N · 6.25) was determined by the Kjeldahl method (6), and the residual glucosinolates and their breakdown products were determined according to the method of Wetter and Youngs (7), based on the ultraviolet absorbance of the glucosinolate hydrolysis products, thioureas, and oxazolidine-2-thione.

EXPERIMENTAL PROCEDURES

Oil equilibrium in a CH_3OH/H_2O/NaOH-hexane system. Different amounts (1 to 31 g) of crude canola oil were contacted

with constant and equal volumes (100 mL) of 0.08% (w/w) NaOH in 95/5% (vol/vol) CH_3OH/H_2O, and hexane. The two-phase solution was agitated for 2 h at room temperature in a wrist-action shaker. After agitation, the two phases were separated by a separatory funnel. After separation, the two phases were weighed, and their oil contents were determined by evaporating the solvents in a rotary vacuum evaporator.

The residue from the polar phase contained both oil and NaOH, which is nonvolatile. The amount of oil in the residue was calculated by subtracting the weight of NaOH in the residue from the total weight of the residue.

Meal preparation. Ground meal for equilibrium investigations was prepared in the following manner: 1.2 kg mixed canola seed and 0.08% (w/w) NaOH in methanol containing 5% (vol/vol) water (CH_3OH/H_2O/NaOH) were manually fed into a Szego mill (General Comminution Inc., Toronto, Ontario, Canada) at a solvent-to-seed ratio (R) of 2.5 (vol/wt). The slurry was collected and diluted to $R = 3.5$ (vol/wt) with CH_3OH/H_2O/NaOH that had been used to rinse the Szego mill. The resulting slurry was vacuum-filtered through Whatman No. 1 filter paper (Maidstone, England). The meal was washed twice with methanol, each time at an approximate solvent-to-meal ratio of one (vol/wt), and air-dried overnight.

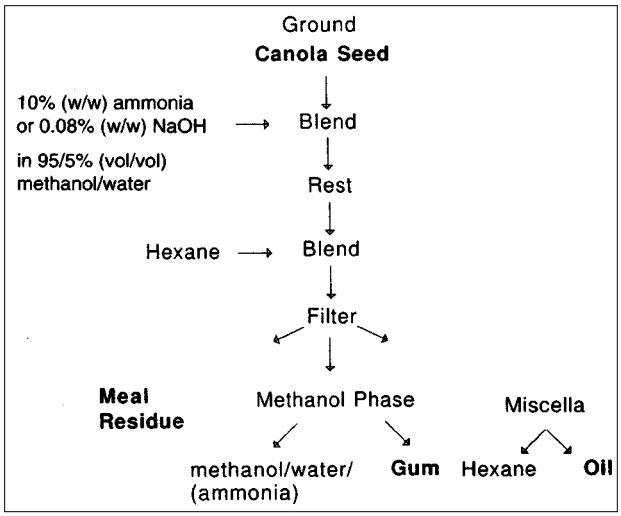
Oil equilibrium in a meal-hexane system. Prepared ground meal (30 to 50 g) was contacted with different amounts of hexane, to vary the solvent-to-meal ratio [R_{hexane} = 2 to 40 (vol/wt)], in an Osterizer blender (Sunbeam Corp., Toronto, Ontario, Canada). The blending time was kept constant at 2 min. After blending, the slurry was vacuum-filtered through Whatman No. 42 filter paper. The filtrate (miscella) was collected, and its oil content was determined by evaporating the hexane in a rotary vacuum evaporator. The meal residue was air-dried overnight, and its oil content was determined by further hexane extraction in a Soxhlet apparatus.

The oil is distributed between the solid and liquid phases. To accurately determine the total amount of oil extracted into the liquid phase during blending, all miscella should be removed from the solids. Unfortunately, this is not possible, because filtration produces a solid that contains 50–60% liquid. To accurately determine the amount of oil extracted into the liquid phase, the extracted oil in the miscella that remained with the filtered meal had to be determined. This was done by weighing the wet filtered meal, evaporating the hexane by air-drying overnight, and reweighing. The amount of hexane evaporated from the wet meal was calculated by difference. The hexane and oil contents in the filtered miscella were measured, and the composition of the miscella retained with the meal must be the same. Based on the concentration of oil in the miscella, the amount of extracted oil retained in the meal during the filtration was calculated.

Oil equilibrium in a meal–CH_3OH/H_2O/NaOH–hexane system. Prepared ground meal (30 g) was contacted with a constant volume (200 mL) of 0.08% NaOH in methanol, containing 5% (vol/vol) water, and different volumes (80 to 500 mL) of hexane in an Osterizer blender. The blending time was kept constant at 2 min. After blending, the slurry was vacuum-filtered using Whatman No. 42 filter paper. The meal residue was air-dried overnight, and its oil content was determined by Soxhlet extraction with hexane. The filtrate was separated into polar and nonpolar phases in a separatory funnel. The oil content in the miscella was determined by evaporating the hexane in a rotary vacuum evaporator.

The amount of extracted oil deposited on the filtered meal was calculated as mentioned previously. The amount of total solvent in the meal was calculated from the difference in weight between the wet and dry meal. The amount of hexane in the meal was then calculated based on the assumption that the weight fraction of hexane-to-total solvent in the meal was equivalent to the weight fraction initially added. Only the amount of extracted oil deposited on the filtered meal from the miscella was taken into account. The deposited oil from the polar phase was assumed to be relatively negligible.

Two-phase solvent extraction. The experiments were performed as described by Rubin *et al.* (2) with some modification (Scheme 1). Mixed canola seed (30 g) was ground for 1.5 min in an Osterizer blender and blended for 2 min with 200 mL of either a 10% solution (w/w) of ammonia or a 0.08% solution (w/w) of NaOH in methanol with 5% water (vol/vol). After a quiescent period of 15 min, 200 mL hexane was added, and the mixture was again blended for 2 min. The meal was separated by vacuum-filtration through Whatman No. 40 filter paper (Maidstone, England), rinsed three times with methanol, each time with a 50-mL portion, and air-dried overnight. The meal was further extracted with hexane in a Soxhlet apparatus to determine residual oil. The filtrate was separated into polar and nonpolar phases in a separatory funnel. The nonpolar phase was evaporated under vacuum in a rotary evaporator to recover the oil. The polar phase was re-extracted four times with hexane at a polar phase-to-combined hexane ratio of two (vol/vol) to recover additional oil. The polar phase was then evaporated under vacuum in a rotary evaporator to recover the gums. For each run, a material



SCHEME 1

balance was calculated, and the protein and glucosinolate contents of the final meal were determined.

RESULTS AND DISCUSSION

Oil equilibrium in hexane–$CH_3OH/H_2O/NaOH$. Linear regression analysis, by using Lotus 123 version 2.2 (Lotus Development Corp., Cambridge, MA), related the equilibrium distribution of crude canola oil between hexane and $CH_3OH/H_2O/NaOH$ (Fig. 1):

$$Y = 49.2X \quad [1]$$

where Y = (g oil/g hexane) · 100 and X = (g oil/g $CH_3OH/H_2O/NaOH$) · 100. The results fit the equation with a regression coefficient $r^2 = 0.988$.

The slope of the line, the ratio of the solubility of oil in hexane-to-$CH_3OH/H_2O/NaOH$, represents the partition (or distribution) coefficient of canola oil in the two phases. The high value represents a large concentration driving force for mass transfer. In our extraction process, the partition of oil between the two phases allows simultaneous contact with both phases because it results in little oil dissolving in the methanol phase, and thus, nearly all of the oil can be recovered from the hexane phase by conventional means.

Equilibrium oil extraction in meal–hexane. As the hexane-to-seed ratio (vol/wt) (R_{hexane}) increased, the oil content in the meal and hexane both decreased (Fig. 2). A higher R_{hexane} provided a larger concentration driving force for extraction. During blending, high R_{hexane} also resulted in smaller median particle size, which increased surface area, decreased solvent penetration path lengths, and improved oil transfer into the miscella (8).

The asymptotic nature of the curves may be explained on the basis that, after grinding, the oil is distributed into three fractions (9): grinding ruptures some of the cells of the seed, and the oil is forced out of the seed to form a layer on the surface where it is loosely held; oil in partially ruptured cells or in the capillary channels formed by ruptured or partially ruptured cells which is removed with difficulty; and unextracted oil.

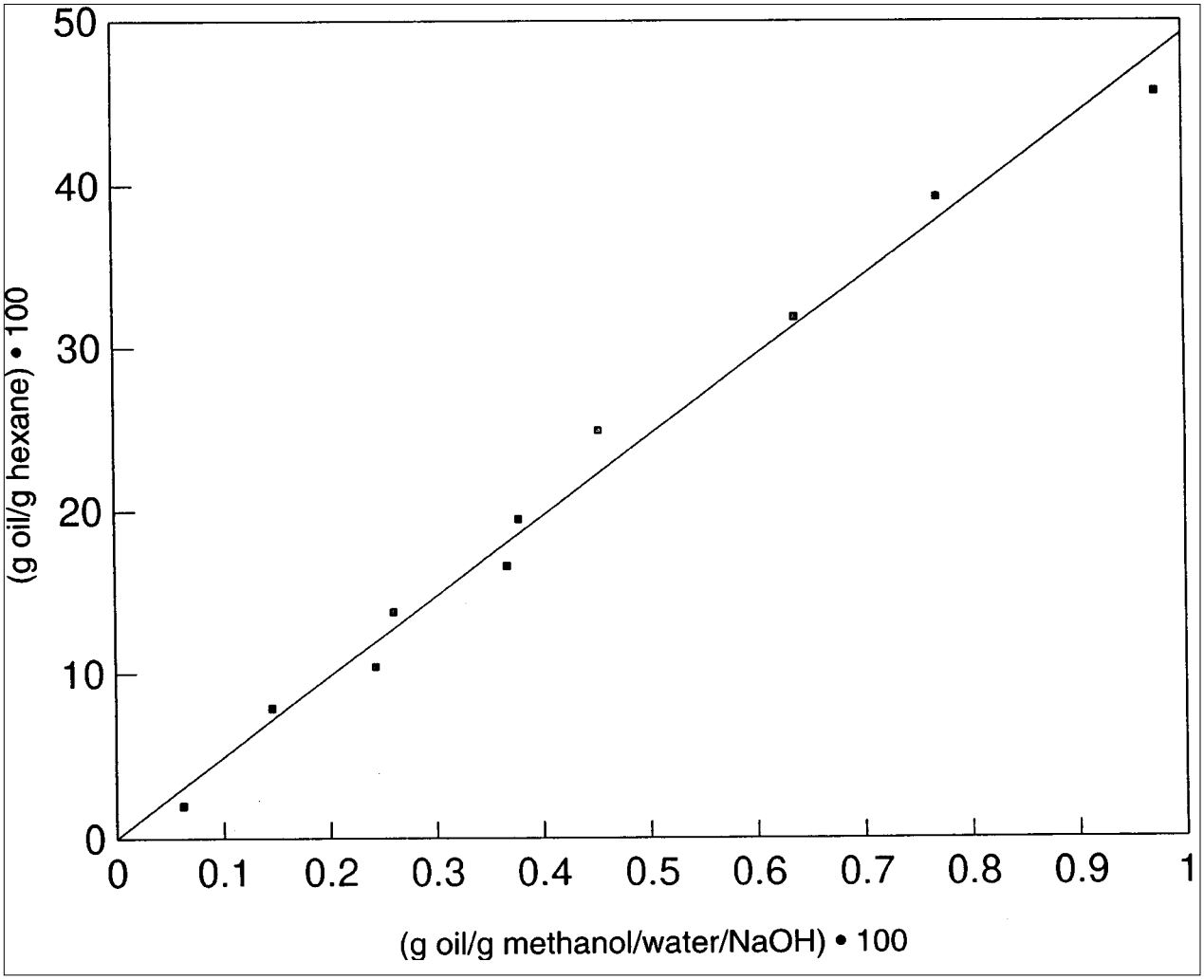


FIG. 1. Partition coefficient of canola oil.

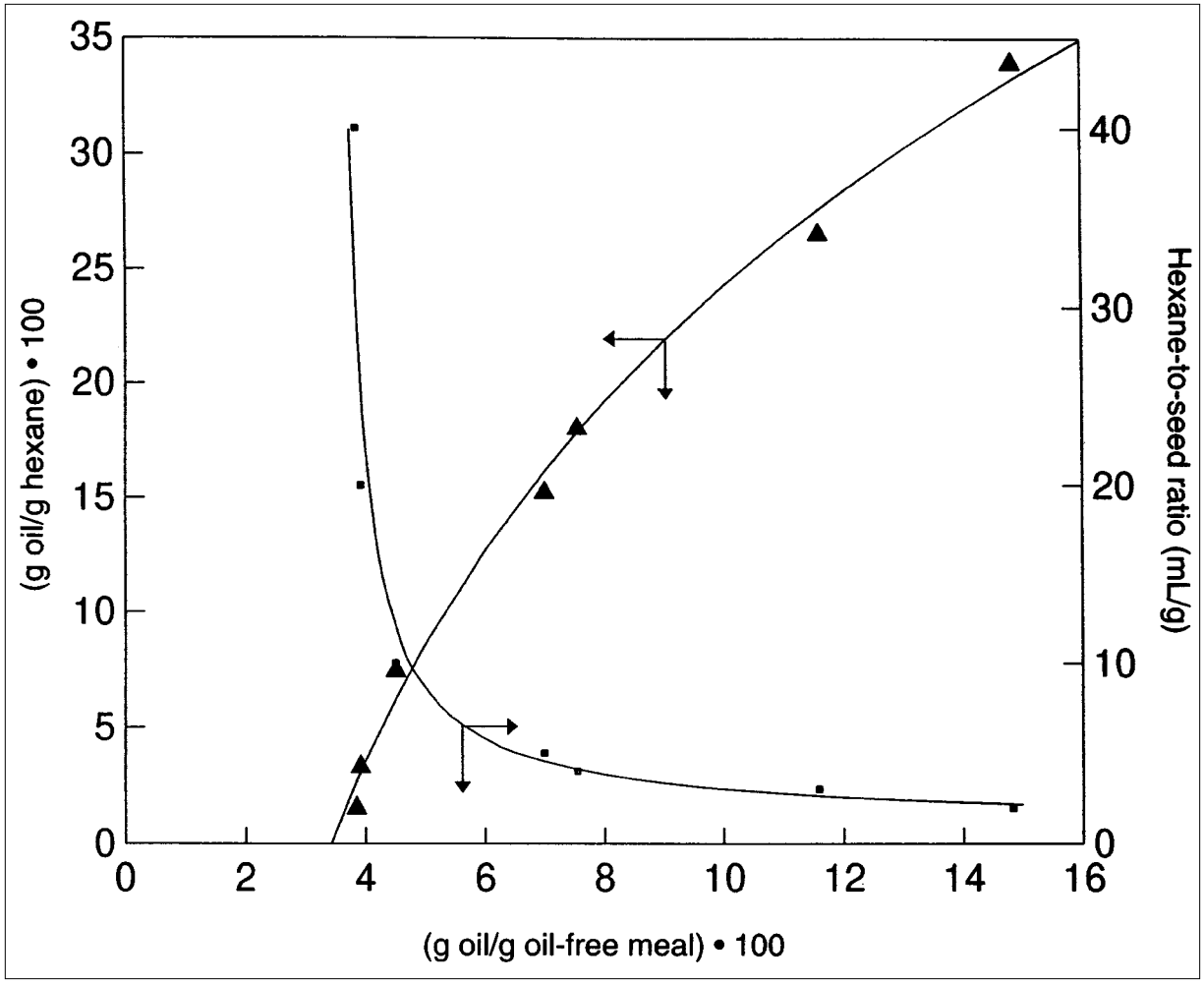


FIG. 2. Equilibrium oil extraction in a meal–hexane system.

The first fraction of oil was easily extracted, mainly by simple washing (10). Increasing R_{hexane} up to a certain limit (R_{hexane} = 10) provided a larger concentration driving force for extraction, and the residual oil content of the meal decreased linearly. Removal of oil from the second fraction of oil was more difficult and probably occurred primarily by diffusion (10). The composition of the extracted material changed as the extraction proceeded with the last fractions containing increasing amounts of slowly soluble nonglyceride material (11). Karnofsky (12) also reported that phosphatides in the cell are located at interfaces and block access of hexane to the oil, making extraction slow compared to washing. The change in the amount of this portion of oil, extracted per unit increase in R_{hexane}, decreases with increasing R_{hexane}. Further extraction requires a longer time, higher temperature, or more contact stages. The maximum amount of oil extracted in a single stage with a contact time of 2 min corresponded to about 3.4% residual oil content in the meal. This final fraction of unextracted oil is likely physically bound to the protein (13,14) or is dissolved in hexane diffused into the intact cells and is in equilibrium with the miscella.

Equilibrium oil extraction in meal–CH_3OH/H_2O/NaOH–hexane. In a three-phase system, at high R_{hexane} (CH_3OH/H_2O/NaOH-to-seed ratio = 6.7 mL/g), the combined effect of a larger concentration driving force for mass transfer and a smaller median particle size resulted in improved oil extraction and, hence, lower residual oil contents in the meal (Fig. 3).

The shape of the curve may again be explained by the mechanism involved in the extraction process. Up to R_{hexane} = 5, most of the oil is removed by simply washing from the solid surface to the solvent. At higher R_{hexane}, more of the remaining oil is extracted by diffusion from within the solid to the solvent (10).

The relationship between the oil content in hexane and the residual oil content in the meal in the presence of

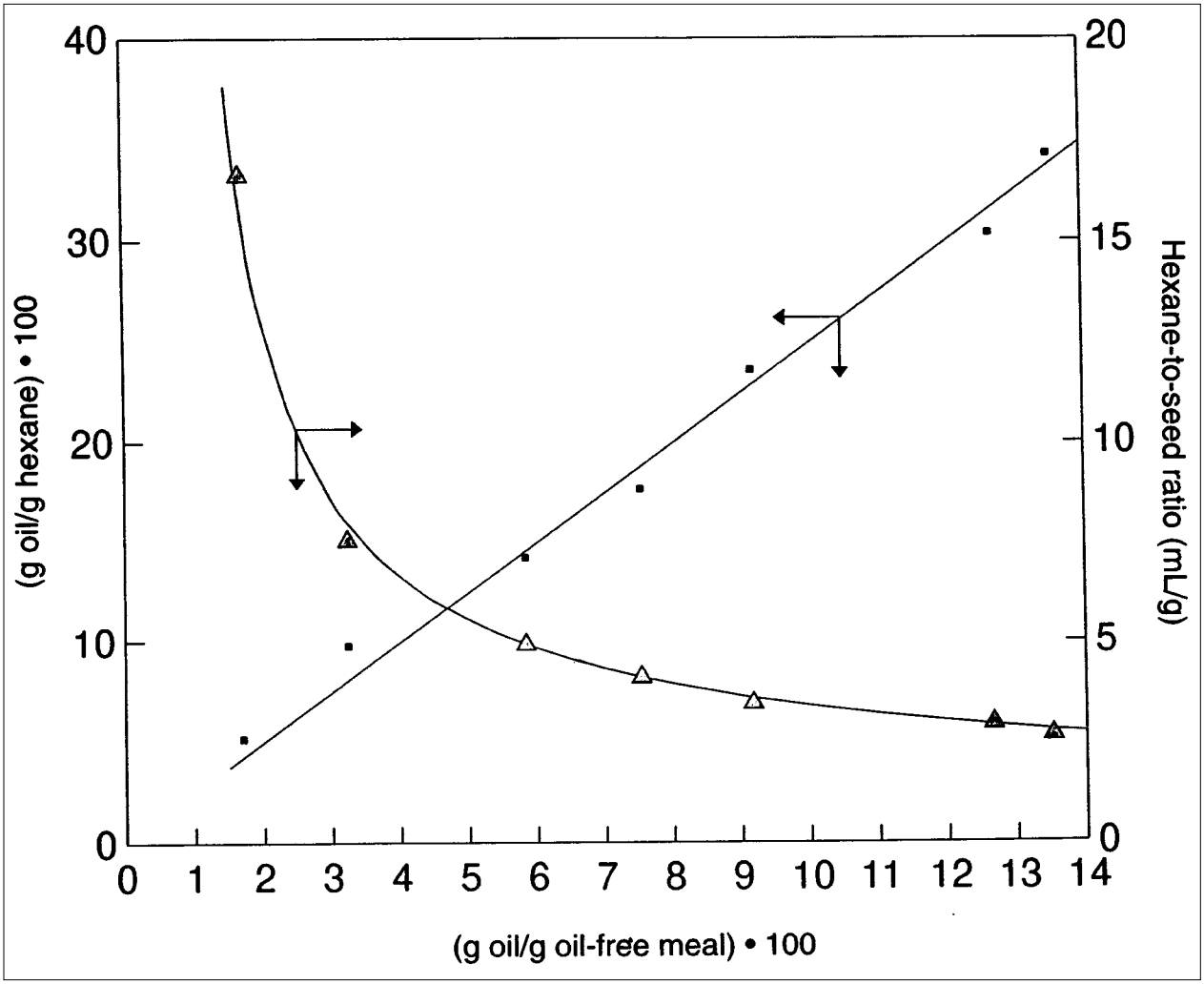


FIG. 3. Equilibrium oil extraction in a three-phase system.

$CH_3OH/H_2O/NaOH$ was (Fig. 3):

$$Y = 2.49X \quad [2]$$

where Y = (g oil/g hexane) · 100 and X = (g oil/g oil-free meal) · 100. The results fit the equation with a regression coefficient $r^2 = 0.989$.

A comparison of the meal–hexane and three-phase equilibrium data (Fig. 4) shows that, up to $R_{hexane} = 4$, the two-phase and three-phase extracted meals had similar residual oil concentrations at constant R_{hexane}. However, hexane-insoluble phospholipids, dissolved in the methanol phase, caused an increase in the residual oil concentration of the three-phase extracted meals. The amount of lipids extracted was greater in the three-phase extraction than in the two-phase extraction. At $R_{hexane} > 4$, the presence of $CH_3OH/H_2O/NaOH$ clearly improved oil recovery. Nearly all of the oil was recovered in a single-stage contact between the Szego mill ground seed and the two-solvent phases.

As mentioned previously, the last fractions of extracted material contain increasing amounts of slowly soluble phosphatides, which are located at cell interfaces and block access of solvent to the oil. In our extraction process, initially grinding the seed with $CH_3OH/H_2O/NaOH$, followed by simultaneous extraction with $CH_3OH/H_2O/NaOH$-hexane, removed these phosphatides, thus allowing the last portion of the oil to be extracted faster and with less difficulty.

It has been reported earlier that methanol–ammonia ruptures cells in both single-celled organisms and in oilseeds. It is likely that $CH_3OH/H_2O/NaOH$ solution had a similar effect: rupturing membranes, left intact by grinding, to allow more thorough oil extraction (Fig. 5). It also dissolved or displaced oil from the seed matrix and made it more available for hexane extraction. The high density and surface tension of methanol, compared to that of hexane, allowed methanol to better penetrate the capillary channels of the seed matrix (15).

In solid–liquid extraction, diffusion in the solid is usually rate-controlling. From Equations 1 and 2, the equilibrium concentrations of oil in the methanol phase and meal can be correlated as follows:

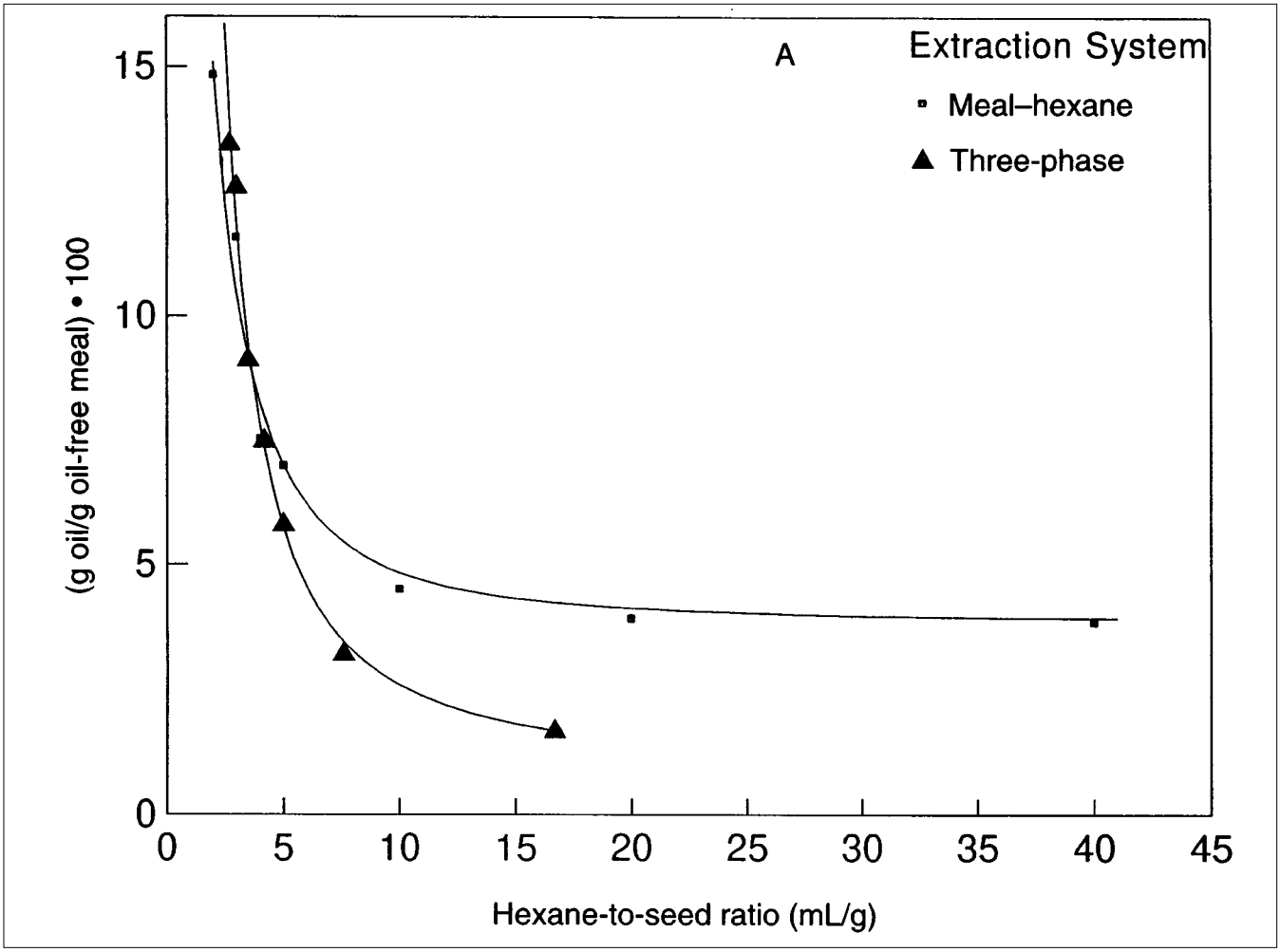


FIG. 4. Comparison of meal–hexane and three-phase equilibrium oil extractions, equilibrium oil content..

$$Z = 0.051X \quad [3]$$

where, Z = (g oil/g $CH_3OH/H_2O/NaOH$) · 100 and X = (g oil/g oil-free meal) · 100.

When considering liquid–liquid extraction, from the equation relating the overall and individual mass transfer coefficients (in interphase mass transfer) and the high partition of oil (Eq. 1), the raffinate phase resistance is equal to the overall resistance, and mass transfer in the liquid–liquid system is raffinate phase-controlled.

The equilibrium measurements suggested that the $CH_3OH/H_2O/NaOH$–hexane system is suitable for the extraction of oil and deserved further study.

Diosady and coworkers (8,16) showed that Szego mill-ground seed required 30 s to 1 min to reach equilibrium. For these extraction experiments, the system was therefore assumed to have reached steady state after a blending time of 2 min. Longer blending times were not used to avoid the heat generated by the blending process from raising the temperature of the slurry and affecting the oil equilibrium results.

Two-phase solvent extraction. A mass balance showed that almost all mass was accounted for in the oil, meal and gum (residue in the methanol phase) phases (Table 1). The observed losses were reasonable and due to the difficulties in the quantitative transfer of slurries and cakes from one unit operation to another. The extracted gum material consisted of carbohydrates, phospholipids, free fatty acids, nonprotein nitrogen and phenolics, as well as glucosinolates and their breakdown products (17).

Most of the oil was extracted into the hexane phase, with a small amount dissolving in the methanol phase (Table 2). Less oil was found in the $CH_3OH/H_2O/NaOH$ solution than in the $CH_3OH/H_2O/NH_3$ solution. More of the total oil recovered remained in the NH_3-treated meal than in the NaOH-treated meal. The greater oil loss after the NaOH treatment may have been due to a hydrolysis reaction (saponification) between NaOH and the triglycerides The higher gum yield (Table 1) from the NaOH treatment was probably due to the presence of oil hydrolysis products and not necessarily due to the increased dissolution of undesirable solid materials from the seed.

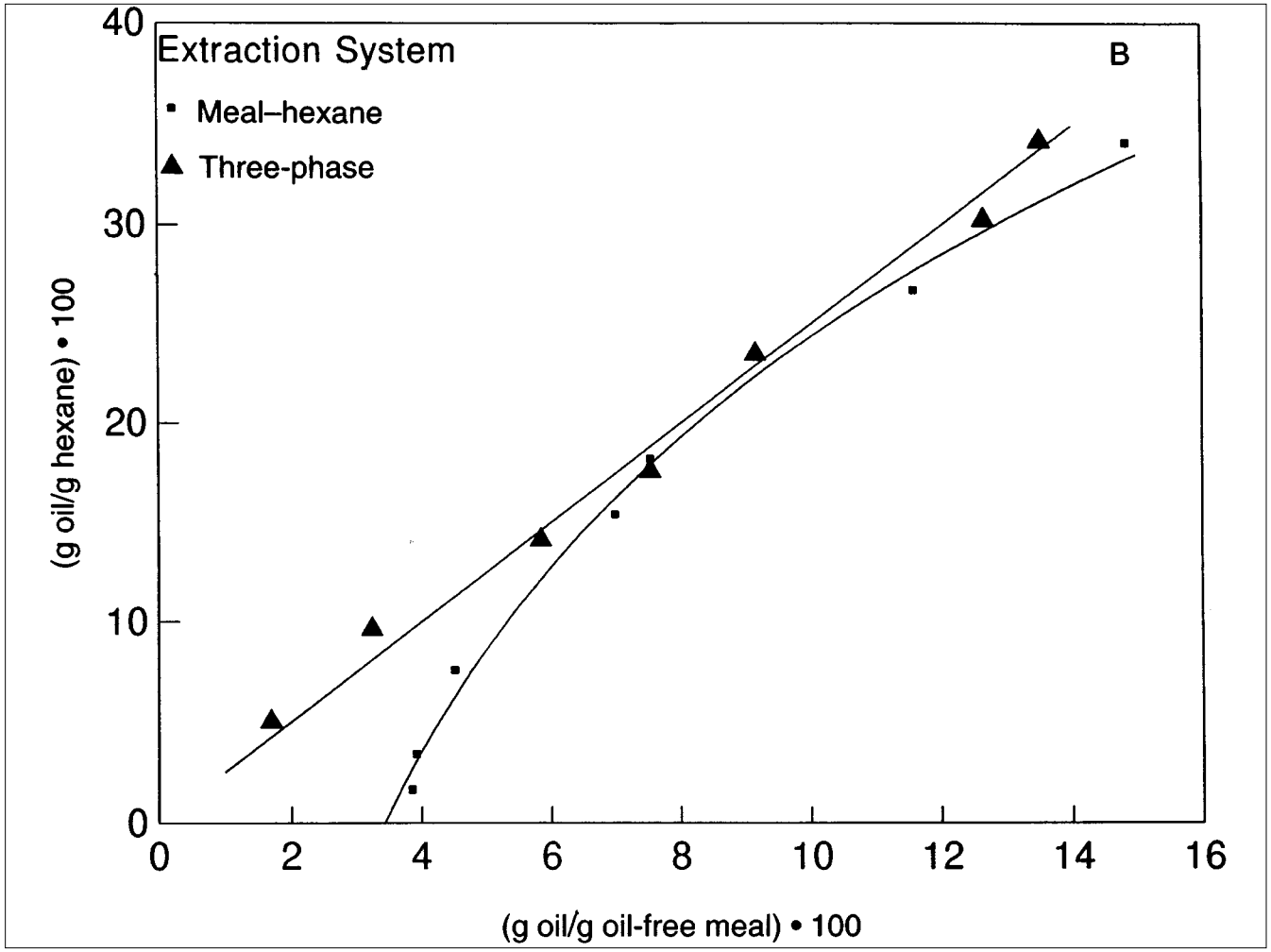


FIG. 5. Comparison of meal–hexane and three-phase equilibrium oil extractions, phase distribution curves.

The crude protein contents and the corresponding protein recoveries of the NH_3- and NaOH-treated meals revealed that the $CH_3OH/H_2O/NaOH$ solution likely dissolved more protein than the $CH_3OH/H_2O/NH_3$ solution. Crude protein dissolved in the $CH_3OH/H_2O/NH_3$ phase corresponded closely to the nonprotein nitrogen (4), indicating that the further increase in nitrogen extraction by $CH_3OH/H_2O/NaOH$ was due to protein solubilized by the NaOH-containing polar phase. The two-phase solvent extraction increases the protein content of the meals compared to conventional hexane-extracted meals due to the dissolution of polar compounds out of the seed by the methanol phase.

The NaOH treatment was less effective in extracting the glucosinolates (Table 3). The $CH_3OH/H_2O/NaOH$ solution removed only about 50% of the glucosinolates present in the seed. The use of $CH_3OH/H_2O/NaOH$ as a washing solution (after filtration), as opposed to CH_3OH alone, may help reduce the glucosinolate content in the meal somewhat further (18). The glucosinolate content of the $CH_3OH/H_2O/NH_3$-treated meal was below the detection limit of the analytical

TABLE 1
Effect of NH_3 and NaOH in the Polar Phase on Product Distribution

	Yield (% of seed, dry basis)	
	NH_3[a]	NaOH[b]
Oil	44.9 ± 0.3	43.4 ± 0.7
Gum	10.7 ± 0.4	12.3 ± 1.8
Meal	43.8 ± 0.4	45.4 ± 0.5
Total	99.4 ± 0.6	101.1 ± 2.0

[a]Results expressed as mean ± SD of triplicates.
[b]Results expressed as mean ± SD of four replicates.

TABLE 2
Effect of NH_3 and NaOH in the Polar Phase on Oil Distribution

	Oil content (% of total seed oil)	
	NH_3[a]	NaOH[b]
Hexane phase	83.6 ± 0.7	83.4 ± 1.3
Methanol phase	2.2 ± 0.2	1.3 ± 0.0
Meal	11.0 ± 0.2	8.8 ± 0.6
Error	3.2 ± 0.8	6.5 ± 1.4

[a]Results expressed as mean ± SD of triplicates.
[b]Results expressed as mean ± SD of four replicates.

TABLE 3
Effect of NH_3 and NaOH in the Polar Phase on Protein and Glucosinolate Contents in the Meal and on Protein Recovery

Treatment	Protein content[a]	Protein recovery[b]	Glucosinolate content[c]
NH_3	48.8 ± 0.2	94.0 ± 3.4	≤1.8
NaOH	46.0 ± 0.2	91.8 ± 3.4	4.20 ± 0.09

[a]Percentage of meal, dry basis; results expressed as mean ± SD of triplicates.
[b]Percentage of total in seed, dry basis.
[c]μmol per g of air dry, oil-free meal; results expressed as mean ± SD of eight replicates.

method employed, indicating at least 78% glucosinolate removal.

The oil-free meals produced by both treatments were free-flowing, light in color, and bland in taste. The oils produced by both treatments were green in color, presumably due to the presence of chlorophyll.

The use of NaOH makes solution preparation and recovery easier and eliminates the danger of exposure to ammonia, a toxic gas. This advantage is offset by the lower oil recovery and higher residual glucosinolates. Tests on a semipilot scale with NaOH in the polar phase will be reported separately (19).

ACKNOWLEDGMENTS

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