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Solvent Extraction: Kinetic Study of Major and Minor Compounds

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Abstract The effects of temperature and contact time on lipid extraction from sunflower collets was investigated in a batch extractor with hexane as solvent. The total removed material varied in quantity and composition due to changes in temperature and contact time. Higher temperatures enhanced oil extraction as well as increased the tocopherol and phospholipid contents of the oil. The kinetic data for triglycerols, phospholipid and tocopherols extraction were interpreted by using an equation that considers extraction as the sum of two components: diffusion and washing. Effective diffusion coefficients for oil, tocopherols and phospholipid at different temperatures were determined. Control of temperature and contact time are essential to obtain good quality oil and reduce refining costs. Extraction at 60 °C and short contact times (30 min) obtained high oil yield (98%) accompanied by significant tocopherol extraction (>99%) and reduced phospholipid extraction (66%).

Keywords Effective diffusion coefficients · Extraction · Sunflower · Hexane extraction · Minor compounds · Tocopherols · Phospholipids

List of symbols

A	Model constant
$A_1,\ldots, A_n$	Model coefficients
B	Model constant
$B_1,\ldots, B_n$	Model coefficients (1/s)
c	Solute concentration (kg solute/kg miscella)
D	Diffusivity (m^2/s)
D_o	Constant in Arrhenius equation (m^2/s)
D_e	Effective-diffusion coefficient (m^2/s)
E_a	Activation energy (kJ/mol)
$J_0\ (R\ \lambda_1)$	Bessel function
L	Collet length (m)
M_t	Solute mass diffused at time t (kg of solute/kg of inert solid)
M_0	Solute mass already diffused during the washing stage (kg solute/kg inert solid)
M_{inf}	Solute mass diffused at infinite time (kg solute/kg inert solid)
r	Radial coordinate (m)
r^2	Correlation coefficient
R	Collet radius (m)
R_g	Gas constant (kJ/[mol K])
t	Diffusion time (s)
t_0	Time corresponding to the washing stage (s)
T	Absolute temperature (K)

Greek letters

λ_1	Non-zero roots of the Bessel function (1/m)

Subscripts

1, 2,…, n	Series terms
0	Washing stage
Inf	Infinite time
t	At time t

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Introduction

Solvent extraction is the primary means of extracting vegetable oil from oleaginous materials. Pretreated oilseeds (porous solid matrix) are contacted with pure solvent or a

solvent/oil mixture (miscella). As a result, the oil is transferred from the solid matrix to the fluid medium [1]. Commercial quality hexane (45–90% *n*-hexane) is usually employed as it gives larger oil yields than pure *n*-hexane. This is probably due to the presence of other constituents, such as methyl pentane [2, 3].

Numerous theories have been proposed to explain the mechanism of oil recovery by solvent from oilseed cakes and flaked and/or expanded oilseeds [4–10]. In solvent-extraction both diffusion in the solid matrix and convection in the surrounding liquid miscella need to be considered. External mass transfer coefficients can be calculated from experimental correlations, usually expressed in terms of dimensionless numbers, as a function of liquid properties and flow conditions through the extractor. Instead, effective liquid–solid diffusion coefficients should be determined for each particular product since they depend on the structure and composition of the solid matrix. Therefore, the diffusion coefficient is an important transport property that permits predicting global coefficients of mass transfer and design mass transfer equipment such as industrial extractors.

The effects of the nature of the solvent, particle size or flake thickness, extraction temperature, and moisture on extraction yield have been demonstrated. Molecular diffusion by itself does not explain experimental results [5, 11]. Moreover, some research [8, 12] has shown that the mechanism for extracting olive foot cakes and ground oilseeds comprises two stages. The first refers to the oil at the particle surface that is recovered by simple washing, while the second corresponds to a diffusion process that could involve two mechanisms: slow diffusion from broken cells and very slow diffusion from intact cells.

Temperature is also an important factor during oil extraction because a higher temperature not only decreases solvent viscosity, but also oil viscosity and therefore the miscella viscosity. Moreover, the solubility of the extractant increases. Lower viscosity and higher solubility result in a higher extraction rate. Temperature influences not only the extraction rate, but also the proportion of non-oil lipids and non-lipid components in the crude oil [13]. It is well-known that the oil removed initially is of higher quality than the smaller proportion which is extracted with difficulty in the final extraction stages. The majority (about 80%) of the oil is removed rapidly, but the last fraction is extracted slowly and with increasing difficulty [14]. Consequently, the composition of the extracted material changes as the extraction proceeds, from nearly pure triglycerides in the first fraction to portions containing increasing amounts of slowly soluble non-triglyceride compounds. Up to now, oil extraction research has focused on obtaining the higher oil yield and explaining theoretically triglyceride removal without considering minor compounds. Some of these minor compounds have prooxidant or antioxidant properties (e.g., tocopherols, metals and free fatty acids [15]), and others must be removed in the refining process (e.g., free fatty acids, phospholipids and waxes).

In general, vegetable oils are considered to be a single component since all the triglycerides are miscible in hexane. Even though studies focused on extraction of minority compounds are limited, it has been shown that samples high in moisture content extract more phosphatides [14]. Few studies have taken the extractability of minor compounds into account. This knowledge could contribute to more effective design of oil solvent extraction processes. Lower extraction efficiency may give higher quality oil, reducing the level of substances to be removed during refining and the oil loss in degumming and winterization.

The aim of this paper was to determine the extraction kinetics of the most important oil components in sunflower collets in a batch reactor using hexane as solvent. The present study is focused on the determining effective liquid–solid diffusion coefficients necessary to design industrial percolation extractors. The transport phenomena were analyzed and model equations were proposed to explain triglyceride, tocopherol and phospholipid extraction.

Materials and Methods

Raw Materials

All experimental determinations were made with sunflower collets (porous cylinders obtained from pressed sunflower cake by expanding), which were kindly provided by a local factory. The collets were stored in the dark at 5 °C under nitrogen atmosphere until used in extraction experiments. The oil content of the solid was determined by an exhaustive extraction with analytical reagent *n*-hexane (90%, bp 68–72 °C) in a Soxhlet apparatus following the IUPAC standard method 1.122 [16]. The moisture content of the collets was measured by using the vacuum-oven technique according to AOCS method Ba 2b-82 [17]. Determinations were performed in triplicate. To determine the average size of the collets and the dimensions, a sample of 20 collets was randomly selected. The collet dimensions, namely length (L), and radius (R), were measured using a gauge with 0.01 mm accuracy. Physical and chemical properties of the raw material were expressed as the means of n determinations with 95% confidence intervals.

Solvent-Extraction Experiments

The apparatus used to carry out the batch extraction consisted of a 250-mL Pyrex flask with a hemispherical base, magnetically stirred and immersed in a temperature-controlled water bath. The extraction mixture consisted of

approximately 10 g of sunflower collets and 180 mL of *n*-hexane (90%, bp 68–72 °C). A high solvent-to-collet ratio is necessary to make sure that complete extraction is realized. The rate of agitation was kept constant in all experiments, being enough to maintain a well-mixed fluid and keep the particles in suspension.

Experiments were performed at 40, 50 and 60 °C, with extraction times from 0 to 270 min. In addition, equilibrium tests at the three mentioned temperatures were completed at 960 min (considered as infinite time). All the extractions were carried out in triplicate. At the end of the contact time, the flask contents were immediately filtered, and the miscella was concentrated by means of a rotary evaporator. Traces of solvent remaining were removed with a nitrogen stream to achieve constant weight.

Minor Components Analyzes

The tocopherols content was measured by an HPLC instrument equipped with a fluorescence detector using AOCS method Ce 8-89 [17]. Quantitative determination of phospholipids was carried out by enrichment using a diol solid-phase extraction cartridge (J.T. Backer Inc., Phillipsburg, NJ, USA) and subsequent analysis by HPLC–UV [18]. A Waters 600E HPLC (Waters Associates, Milford, MA, USA) system and a Lichrosorb SI-60, (250 × 4 mm, 5 μm particle size) column (Merck, Darmstadt, Germany) were used for both determinations.

Microscopy

Longitudinal sections of collets were sliced with a razor blade, after the collets were plunged into liquid nitrogen to maintain the structure. The slices were adhered to a cover slip, coated with a gold thin film in a sputter coater (Pelco 91000) and observed in a scanning electron microscope (model 35 CF, Jeol, Tokyo, Japan) at 7.0 kV using 5,000× magnification.

Mathematical Model

When a porous solid containing a liquid solute is brought into contact with a solvent liquid, interdiffusion of molecules of the two liquids follows. This diffusion can be defined by Fick's law, which is valid for diluted binary systems (i.e., a solute with a large proportion of solvent) in the so-called non-stationary state flow,

$$\frac{\partial c}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\, D\, \frac{\partial c}{\partial r}\right), \tag{1}$$

where c is the concentration of solute, t is the time, r is the radius of the cylinder, and D is the diffusion constant also called diffusivity.

The solution of Fick's law for a cylindrical particle suspended in a homogeneous medium of constant concentration and without volume restriction (i.e., high solvent-to-collet ratio) was described by Crank [19]:

$$\frac{M_t}{M_{\inf}} = 1 - \sum_{n=1}^{\inf} A_n\, \mathrm{e}^{(-B_n t)}, \tag{2}$$

where M_t and $M_{\inf}$ are the mass of substance that has diffused at time t and at infinity time (kg oil/kg inert solid), t is the diffusion time (s), A_n and B_n are the coefficients of the model that involve the diffusion coefficient and depend on the geometric form of the particle.

When pretreated oilseeds are contacted with fresh solvent not containing oil, a series of phenomena takes place as the washing or eluting of the superficial oil. The solvent soaks into the porous solid modifying the solid structure and causing miscella displacement for non-diffusive mechanisms (viscous and capillary flow). These phenomena happen almost instantaneously and help to eliminate part of the oil during the initial period. Considering this initial stage of washing, we propose the utilization of the following diffusive modified model to explain the extraction process [8]:

$$\frac{M_t}{M_{\inf}} = 1 - \left(1 - \frac{M_0}{M_{\inf}}\right) \sum_{n=1}^{\inf} A_n\, \mathrm{e}^{[-B_n(t-t_0)]}, \tag{3}$$

where M_0 is the mass of substance that has diffused in the washing stage, and t_0 is the time corresponding to this stage.

For very long time, only the first term in the series is needed:

$$\frac{M_t}{M_{\inf}} = 1 - \left(1 - \frac{M_0}{M_{\inf}}\right) A_1\, \mathrm{e}^{[-B_1(t-t_0)]}, \tag{4}$$

taking into account that:

$$\mathrm{e}^{[-B_1(t-t_0)]} = \mathrm{e}^{(-B_1 t)}\, \mathrm{e}^{(B_1 t_0)}, \tag{5}$$

Equation 4 can be rewritten as:

$$\frac{M_t}{M_{\inf}} = 1 - A\, \mathrm{e}^{(-B_1 t)}, \tag{6}$$

where the A constant is defined as follows:

$$A = \left(1 - \frac{M_0}{M_{\inf}}\right) A_1\, \mathrm{e}^{(B_1 t_0)}, \tag{7}$$

with A_1 and B_1 obtained from the following equations:

$$A_1 = \frac{4}{R^2 \lambda_1^2}; B_1 = D_{\mathrm{e}} \lambda_1^2, \tag{8}$$

D_{e} is the effective diffusion coefficient that involves both washing and diffusion stages. λ_1 are the non-zero roots of the Bessel function of the first kind for zero order,

J_0 (R λ_1) = 0. λ_1 are tabulated in tables of values of the Bessel function.

Phospholipids are the main components of cell membranes. Cytosolic, mitochondrial and vacuolar membranes are composed of phospholipids, among which phosphatidylcholine, phosphatidylethanolamine, and phosphatidylinositol are the most prominent species [21]. Previous evidence indicates that phosphatides are concentrated in the last fraction extracted from soybeans with hexane [22].

We propose Eq. 6 to model separately both triglycerides and minor compounds. Equation 6 is valid only if the flux of soluble material leaving the solid is equal to the flux of soluble material entering the solvent, that is, if there is no limiting layer of concentrated solution around the particles. The values of A and B_1 constants at each temperature were determined by using the nonlinear regression procedure in the Stratigraphics statistical analysis software for PC, Sigma Plot for Windows Version 8.01 (2002 SPSS Inc., Chicago, IL, USA).

Results and Discussion

The raw material (sunflower collets) was characterized physically and chemically giving the following mean values: initial moisture content = 6.73 ± 0.24% dry basis; oil content = 23.49 ± 0.40% dry basis; L = 27.684 ± 5.113 mm; R = 9.444 ± 0.325 mm.

Experimental data (n = 3) of the extraction fraction M_t/M_{inf} at 40, 50 and 60 °C from simple batch extraction experiments are shown in Fig. 1. It shows that 91% at 40 °C, 93.2% at 50 °C and 98.1% at 60 °C of the oil final equilibrium concentration were extracted in 30 min. Figure 1 also shows the predictive model curve. These curves demonstrate that triglyceride extraction increases very quickly at the beginning of the extraction. This behavior could be explained by the fact that this first stage corresponds to the washing process of the oil from the collet surface. The second stage is characterized by an asymptotic increase in yield. Then, extraction only occurs as the result of diffusion, which is an increasingly slow process. A microphotograph of the collet shows how the oil drops are easily accessible (Fig. 2). The application of an external force during pressing breaks cell walls, allowing the oil to escape through the system of pores toward the exterior of the particles. This enforces the idea that rapid extraction takes place first due to oil from ruptured cells, and then, at a slower rate due to diffusion of oil from intact cells. Thus, the predominant mechanism in the extraction process is the washing of oil from the collet surface.

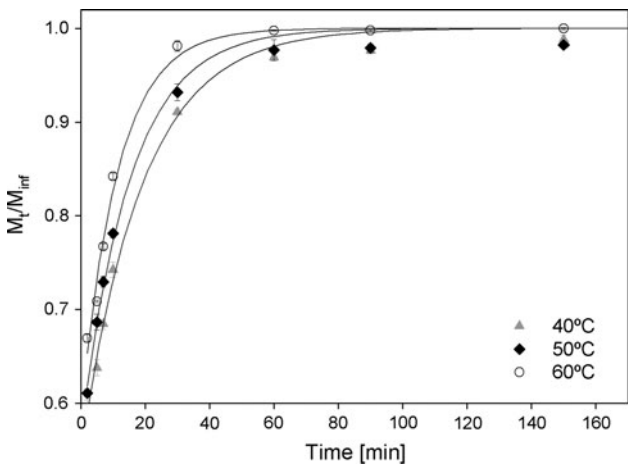

Fig. 1 Oil extraction kinetics of sunflower collets at different temperatures. *Points* represent average values of three experiments, *bars* represent standard deviations, and *lines* correspond to model fitting

Table 1 presents the model coefficients and the effective diffusion coefficient (D_e) for oil extraction. Diffusivity is important for predicting mass transfer coefficients to simulate industrial extractors. Good fits with the experimental data were obtained at the three temperatures evaluated ($r^2 \geq 0.992$). The D_e determined from the model-fitting results varied from 1.356×10^{-8} to 2.247×10^{-8} m^2/s in the temperature range of 40–60 °C. As a result, oil extraction rate increased with temperature. In fact, the rates at which the solvent and miscella soak into the solid and come into equilibrium with the surrounding increase with temperature. This is due to a decrease of the solvent viscosity and the increased solubility of some of the crude-oil components as temperature increased [13]. The dependence of effective diffusion coefficients on temperature is generally described by the Arrhenius equation:

$$D_e = D_0\, e^{-E_a/RT};\ \ln(D_e) = \ln(D_0) - \frac{E_a}{R}\frac{1}{T}, \qquad (9)$$

where D_e is the effective diffusion coefficient, m^2/s; D_0 is a constant m^2/s; E_a is the activation energy, kJ/mol; R_g is the gas constant, $R_g = 8.314 \times 10^{-3}$ kJ/(molK); and T is the absolute temperature [K].

The experimental data lead to the following equation:

$$\ln\left(D_e \times 10^8\right) = 10.984 - 2.6264\left(\frac{1000}{T}\right), \qquad (10)$$

giving E_a = 21.84 kJ/mol, r^2 = 0.9896. This value, which involves both washing and diffusion stages, is in accordance with the typical values reported for the process of diffusion in a liquid (nearly 20 kJ/mol) [23].

Foods contain many components, some of which are extracted more rapidly than others. The diffusivities of trace components are probably mutually independent, but solutes present in large concentration can change diffusivities of other solutes [24]. Between minor components in oilseeds, tocopherols are intrinsically bound to oil body

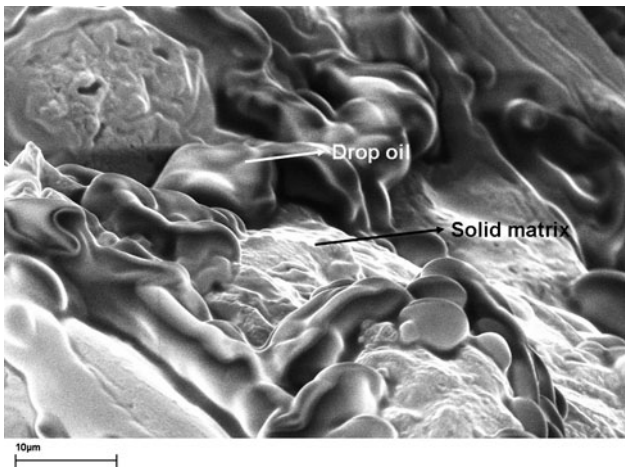

Fig. 2 Transversal section of a sunflower collet showing how the oil drops escape from the system of pores toward the exterior of the particles

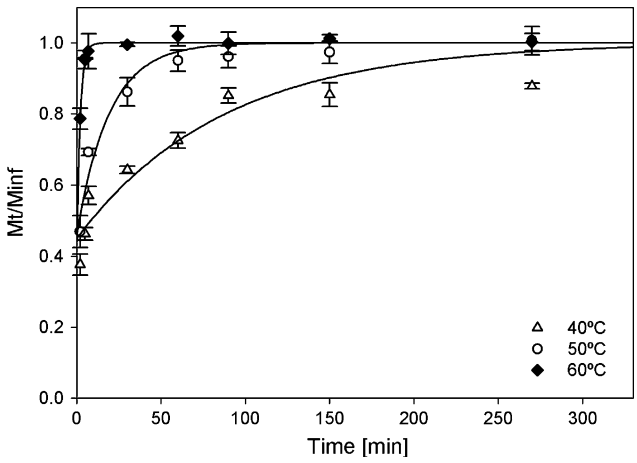

Fig. 3 Tocopherols extraction kinetics at different temperatures, infinite time at 960 min. *Points* represent average values of three experiments, *bars* represent standard deviations, and *lines* correspond to model-fitting curves

Table 1 Model-fitting and effective-diffusion coefficients for oil extraction

Temperature (°C)	$A^a \times 10^2$	$B_1^a \times 10^4$	r^2	$\frac{M_0}{M_{inf}}$	$D_e \times 10^8$ (m^2/s)
40	45.5 ± 1.36	8.79 ± 0.67	0.994	0.3415	1.356
50	43.6 ± 1.44	10.9 ± 0.85	0.995	0.3698	1.683
60	41.3 ± 1.82	14.6 ± 1.32	0.992	0.4023	2.247

[a] Estimated values ± standard error

structures [20]. On the other hand, phospholipids are the main component of cell membranes and their primary function is to maintain the integrity of the cell membrane under different environmental conditions. It should also be noted that when these compounds are associated with oleosin proteins, they are essential for the construction of oil bodies [21]. The increase in mass of tocopherols and phospholipids over time of extraction is shown in Figs. 3 and 4. The percentages of phospholipid extraction at 150 min was 64.8% at 40 °C, 70.4% at 50 °C and 96.2% at 60 °C; the tocopherol extraction curve showed similar behavior to the oil one with the tocopherols almost completely extracted at 40 °C for 90 min, 50 °C for 60 min, and 60 °C for 30 min. The rate of mass transfer increases with temperature, with phospholipids being more difficult to extract than tocopherols. In effect, the 99.5% of tocopherols and 66.5% of phospholipids were removed at 60 °C for 30 min.

The model-fitting results for the minor compounds at the three temperatures are given in Table 2. The correlation coefficients (r^2) indicated good fit for the proposed models ($r^2 > 0.90$). At 40 and 50 °C the values of A obtained for phospholipids were similar to the theoretical ($A_1 = 0.6917$), indicating that the fraction corresponding to the washing stage was relatively small and that the application of the pure diffusive model was reasonable. In contrast, for the curve at 60 °C the magnitude of the initial stage significantly increased. This may be due to the effect of temperature on solubilities and viscosities of the components involved.

The effective diffusion coefficients determined from the model-fitting results vary from 0.2995×10^{-8} to 12.42×10^{-8} m^2/s for tocopherols and from 1.323×10^{-9} to 4.229×10^{-9} m^2/s for phospholipids, in the temperature range of 40–60 °C. The D_e magnitude for tocopherols and phospholipids follows the Arrhenius law, Eq. 9. The resulting equations were:

$$\ln\left(D_e \times 10^9\right) = 62.829 - 19.365\left(\frac{1000}{T}\right), \text{(tocopherols)} \quad (11)$$

$$\ln\left(D_e \times 10^9\right) = 21.611 - 6.0038\left(\frac{1000}{T}\right), \text{(phospholipids)} \quad (12)$$

The correlation coefficients (r^2) were superior to 0.81, and the corresponding activation energies were 161.00 and 49.91 kJ/mol, respectively. The increased mass of tocopherols throughout the time of extraction showed similar behavior to that of oil; however, there were significant differences between their diffusion coefficients and activation energies. It is likely that the long extraction times needed to reach the equilibrium affected tocopherol diffusion since they are affected by light and temperature [25]. To check this, a new kinetic curve was made assuming complete tocopherol extraction was reached when M_t remained practically constant (Fig. 5). The

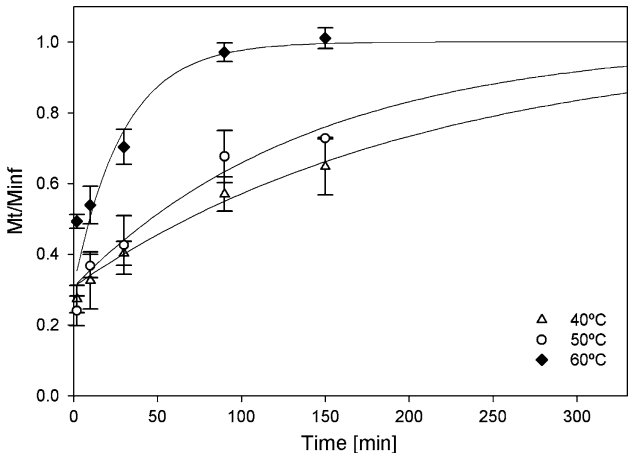

Fig. 4 Phospholipids extraction kinetics at different temperatures. *Points* represent average values of three experiments, *bars* represent standard deviations, and *lines* correspond to model-fitting curves

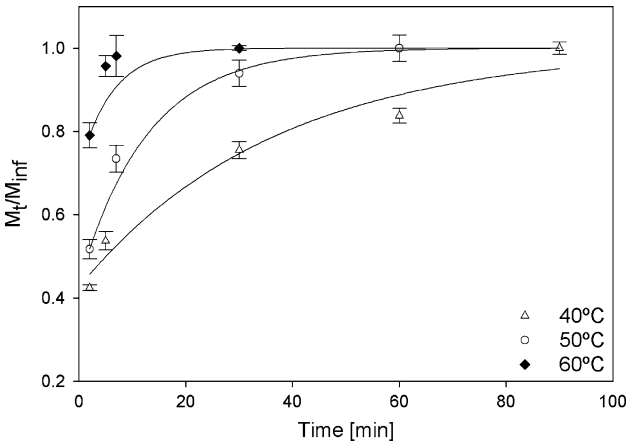

Fig. 5 Tocopherols extraction kinetics at different temperatures. The equilibrium times considered were 30 min at 60 °C, 60 min at 50 °C and 90 min at 40 °C. *Points* represent average values of three experiments, *bars* represent standard deviations, and *lines* correspond to model-fitting curves

model-fitting results are presented in Table 2; the equilibrium times considered were 30 min for the assays carried out at 60 °C, 60 min for 50 °C and 90 min for 40 °C. The effective diffusion coefficients obtained were 0.7006×10^{-8}, 3.066×10^{-8} and 13.24×10^{-8} m^2/s at 40, 50 and 60 °C, respectively. The correlation coefficient (r^2) for the Arrhenius law determined for D_e was 0.98, and the corresponding activation energy was 127.3 kJ/mol. The resulting equation was:

$$\ln\left(D_e \times 10^8\right) = 50.850 - 15.311\left(\frac{1000}{T}\right), \quad (13)$$

Since some tocopherol deterioration was possible, the last assumption leads to a more adequate estimation of tocopherol diffusion coefficients.

Even though activation energies of tocopherols and phospholipids are far away to those obtained for the oil, they are in the range (20–170 kJ/mol) reported for moisture diffusivities in foods [26]. From the point of view of transport phenomena, cells are multiphase systems and the important phases are the cytoplasm, the vacuole, the cell wall and the intercellular spaces. Collets are formed by joined solid particles in porous matrixes. Oil and minor compounds in solid particles are thought to fall into two categories [4]: a free component, which is easily extracted from solid particles (from opened cells), and a bound component (from intact cells), which is extracted with difficulty. As to the extractive liberation of lipids from the intact cell membrane, the following three main steps must be considered: (1) Penetration of the solvent into the tissue; (2) Formation of intracellular miscella; and (3) Diffusion of the extracted material into the external miscella [27]. In the collets, there is also diffusion with flux in matrix pores. Step 2 is accompanied by significant geometrical and permeability alterations as a result of internal pressure within the cotyledon due to intracellular osmotic pressure [27]. The location of the compound in the cell structure,

Table 2 Model-fitting coefficients and effective-diffusion coefficients for tocopherols and phospholipids extraction at 40, 50, and 60 °C

Temperature (°C)	$A^a \times 10^2$	$B_1^a \times 10^4$	r^2	$\frac{M_0}{M_{inf}}$	$D_e \times 10^8$ (m^2/s)
Tocopherols[b]					
40	55.8 ± 4.3	1.94 ± 0.43	0.910	0.1932	0.2995
50	53.9 ± 4.2	8.64 ± 1.89	0.961	0.2201	1.331
60	55.9 ± 8.1	80.5 ± 1.03	0.981	0.1917	12.42
Tocopherols[c]					
40	57.4 ± 3.8	4.54 ± 0.86	0.965	0.1705	0.7006
50	61.3 ± 0.9	19.9 ± 0.59	0.999	0.1139	3.066
60	58.6 ± 2.0	85.8 ± 2.47	0.999	0.1525	13.24
Phospholipids[b]					
40	71.5 ± 1.35	0.86 ± 0.06	0.996	–	0.132
50	65.4 ± 3.76	0.97 ± 0.19	0.964	0.0543	0.149
60	40.2 ± 4.97	2.7 ± 0.94	0.911	0.4184	0.423

[a] Estimated values ± standard error

[b] Equilibrium time at 960 min

[c] Equilibrium time at the time that M_t is almost constant (90 min at 40 °C, 60 min at 50 °C, and 30 min at 60 °C)

differences in miscella composition, and temperature effects on the solubility of minor compounds, among others, may justify differences in the activation energy values.

Kinetic assays carried out in this study will be useful in solvent extraction modeling of oil and its minor components with respect to an industrial percolation extractor. However, because commercial hexane is highly variable in composition, the results obtained in this study using 90% *n*-hexane are conservative since higher oil extractability and lighter color due to the lower presence of some minor components could be expected depending on the presence of other hydrocarbons with lower boiling point [2, 3, 28].

Conclusions

Control of extraction temperature and contact time control are essential in order to obtain good quality oil and reduce refining costs. As a result, batch hexane extractions of sunflower collets at 60 °C and short contact times (30 min) achieved high oil yield (98.1%) accompanied with significant tocopherol extraction (99.5%) and reduced phospholipids extraction (66.5%).

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