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Estimation of the activation energy of carbohydrate polymers blends as selection criteria for their use as wall material for spray-dried microcapsules

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Abstract

A quantitative method for selecting the most suitable biopolymers blends for lipid materials microencapsulation is proposed. Aqueous solutions of carbohydrate polymers blends (gum arabic (GA), mesquite gum (MG) and maltodextrin DE 10 (MD)) were prepared in accordance to a Simplex Centroid experimental design, and a drop of each blend was dried isothermally at 50, 60 and 80 °C in a thermogravimetric analyzer. The effective diffusivity was dependent on moisture content, drop volume shrinkage, and temperature. Drop shrinkage was estimated from polynomial models reported for GA, MG and MD, assuming additive volumes of the blend constituents. Activation energies were calculated considering that the average effective diffusivity followed an Arrhenius-type relationship. The pure biopolymer exhibiting the highest activation energy was MD, followed by MG and GA, respectively. Blends containing 66%GA-17%MG-17%MD and 17%GA-66%MG-17%MD showed higher activation energies than MD, MG and GA suggesting that they better suited for protecting microencapsulated lipids against oxidation.

Keywords: Biopolymer blends; Effective diffusivity; Activation energy; Wall materials

1. Introduction

Spray-drying microencapsulation is a widespread technique used for the preparation of dry, stable additives and flavors (Giese, 1993), that involves a two step procedure: (1) emulsification of a core material such as a lipid with a dense solution of wall material such as a protein, vegetable gum, maltodextrin or modified starch; and (2) atomization and drying of the emulsion (Dziezak, 1988; Watanabe, Fang, Minemoto, Adachi, & Matsuno, 2002). To obtain the greatest effect from these ingredients a proper selection of the wall materials is of the utmost importance so that they 'fit well' with the functional properties desired in the finished product (Pszczola, 1998), such as stability against oxidation, ease of handling, improved solubility, controlled release, and extended shelf-life. Wall materials for spray-drying microencapsulation should have high solubility in water, possess low viscosity at high concentration, be effective emulsifiers and have the capability to form films (Ré, 1998). The selection of wall materials for microencapsulation by spray-drying has traditionally involved trial and error procedures in which the microcapsules are formed, and afterwards they are evaluated for encapsulation efficiency, stability under different storage conditions, degree of protection provided to the core material, surface observation by scanning microscopy, among other evaluations. These procedures involve an enormous range of conditions, are costly and time consuming. Matsuno and Adachi (1993) proposed a method for screening the most suitable wall materials for lipid encapsulation, that takes two steps: (1) emulsification of lipid in a solution of wall material(s), and assessing emulsifying activity by particle size and distribution; and, (2) determination of the rate of isothermal drying of the wall

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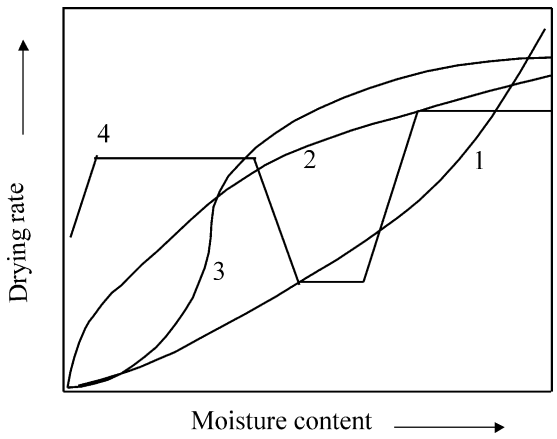

Fig. 1. Schematic characteristic isothermal drying curves of various wall materials.

material(s), obtaining characteristic drying curves (Fig. 1), and selecting those materials that yield concave, upward sloping curves (type 1 curves) in which drying rate decreases rapidly as the water content decreases. These materials tend to form fine, dense, two-dimensional skins immediately upon drying which act as barriers against oxygen transfer, preventing lipid oxidation. Type 2, 3 and 4 curves (Fig. 1) correspond to materials that do not form dense skins at an early stage of drying, and are unsuitable for efficient lipid encapsulation. Characteristic type 2 materials are caseinate and albumin, type 3 materials are low molecular weight saccharides that do not crystallize readily, and type 4 materials are those that form dendritic crystals, such as mannitol (Matsuno & Adachi, 1993). However, not all the materials showing type 1 curves are good emulsifiers, and are not suitable for lipid encapsulation when used alone, so that it is desirable to determine an optimal combination of materials that will provide excellent emulsifying capacity and barrier to oxygen diffusion. In this respect, the Adachi and Matsuno method does not allow for an effective discrimination between materials showing similarly shaped drying curves. This is the case of the biopolymers of carbohydrate nature such as gum arabic (GA), mesquite gum (MG) and maltodextrin (MD). Whereas MD provides good oxidative stability to encapsulated oil, it exhibits poor emulsifying capacity, emulsion stability and low oil retention (Kenyon, 1995), GA has traditionally been the choice material for lipid encapsulation due to its efficient emulsification characteristics (Kenyon, 1995) and oxidative stability provided to oils (Thevenet, 1995). However, GA historically short supplies and high costs have turned industrialists to seek alternative materials for encapsulation such as MG (Vernon-Carter, Beristain, & Pedroza-Islas, 2000) that has a similar structure than GA, but has been reported as being a better emulsifying agent of orange peel oil (Beristain & Vernon-Carter, 1995) and of chili oleoresin (Vernon-Carter, Pedroza-Islas, & Beristain, 1998), or otherwise to blend several of these materials in order to obtain a performance superior to using any one ingredient alone (Kenyon, 1995). Sankarikutty, Sreekumar, Narayanan, and Mathew (1988) reported that a MD-GA blend in a 1:2.3 ratio achieved high levels of cardamom oil retention. Thevenet (1995) reported that GA/MD blends in a 1:1 ratio yielded orange oil powder with almost the same stability to oxidation than pure acacia gum as carrier. MG encapsulated 80.5% of the starting orange peel oil compared to 93.5% by GA, but a 60:40%wt GA to MG blend equaled the performance of pure GA (Beristain & Vernon-Carter, 1995). A 3:2 ratio of MD 10 DE to MG blend retained 84.6% of starting orange peel oil, providing a better encapsulating capacity than either polysaccharide on its own (Beristain, García, & Vernon-Carter, 1999). McNamee, O'Riordan, and O'Sullivan (2001) reported that maltodextrin DE 18.5 replacing 50% of gum arabic rendered soy oil microcapsules with oil retentions slightly above 70%, provided a gum arabic/oil ratio of 1.0 (w/w) was maintained.

Ré (1998) stated that suitable wall materials should have efficient thermal properties (low effective diffusivity and high activation energy) in order to protect the core material upon drying. Diffusivity is a transport property that allows the design and optimization of the drying process, and provides a measure as to how the drying rate proceeds (Zogzas, Maroulis, & Marinos-Kouris, 1994). Diffusivity can be determined by analytical methods (Hernández, Pavón, & García, 2000; Mulet, 1994), numerical methods (Hernández et al., 2000; Kiranoudis, Maroulis, & Marinos-Kouris, 1992), or the regular regime method (Adhikari, Howes, Bhandari, Yamamoto, & Truong, 2002; Báez-González, 2002; Schoeber, 1976). The activation energy provides us with a measure of the necessary energy required for evaporating a mass of water from the material to be dried.

The objective of this work was to determine the activation energy of carbohydrate polymer-blends dried isothermally, to be used as a discriminating parameter for selecting the most suitable mixture as wall material for spray-dried microcapsules.

2. Experimental

2.1. Carbohydrate polymers

Gum arabic (*Acacia senegal*) was purchased from Industria Ragar, S.A. de C.V. (Mexico City, Mexico), mesquite gum (*Prosopis juliflora*) was collected by hand in the Mexican State of San Luis Potosi, both as tear drops, and purified as pointed out by Vernon-Carter et al. (1996). Maltadex 10 (maltodextrin DE 10) was obtained from Complementos Alimenticios S.A. de C.V. (Naucalpan, State of Mexico, Mexico) in the form of a spray-dried powder.

Table 1
Experimental design for obtaining the biopolymers blends

Biopolymer blend code	GA	MG	MD
GA100	100	0	0
MG100	0	100	0
MD100	0	0	100
GA50-MG50	50	50	0
GA50-MD50	50	0	50
MG50-MD50	0	50	50
GA33-MG33-MD33	33.33	33.33	33.33
GA66-MG17-MD17	66	17	17
GA17-MG66-MD17	17	66	17
GA17-MG17-MD66	17	17	66

GA = gum arabic, MG = mesquite gum, MD = maltodextrin DE 10.

2.2. Solution preparation

The three biopolymers GA, MG and MD were mixed following a Simplex Centroid experimental design (Table 1), and 40% weight aqueous solutions of each biopolymer treatment was made with help of a Silverson homogenizer model L4R (Silverson Machines, Ltd., Waterside, Chesham, Bucks., England). The samples were hydrated 24 h before being stored until use at 4 °C to minimize bacterial growth (Rodd, Dunstan, & Boger, 2000).

2.3. Density

The initial density of each biopolymer aqueous solution was determined in triplicate with a Paar digital densimeter model DMA 35 (Anton Paar K.G., Graz, Austria) at 25 °C (Table 2).

2.4. Isothermal drying

A *TA* Instruments model TGA 2950 thermogravimeter (New Castle, DE, USA) was used to obtain the drying curves. Fifteen to thirty mg of each biopolymer solution were placed in the thermogravimeter furnace and dried isothermally at 50, 60 and 80 °C during 90 min, using as purge gas air with relative humidity of 0.008 kg H_2O/kg dry air and flow rate of 100 cm^3/min. The preheating rate to bring the samples from room temperature to the test temperature was varied in order to minimize thermal inertia, sample mass loss and achieve the isothermal test temperature in the shortest time possible (Báez-González, 2002), and were as follows: (a) for 50 °C isothermal temperature, an initial heating rate of 35 °C/min up to 40 °C was applied, followed by a heating rate of 5 °C up to 50 °C; (b) for 60 °C isothermal temperature, an initial heating rate of 40 °C/min until up to 50 °C was applied, followed by a heating rate of 5 °C up to 60 °C; and (c) for 80 °C isothermal temperature, an initial heating rate of 54 °C/min up to 70 °C was applied, followed by a heating rate of 5 °C up to 80 °C. Measurements were done in triplicate.

Table 2
Initial densities of biopolymers 40% weight aqueous solutions at 25 °C

Biopolymer blend code	ρ_0 (kg/m^3)
GA100	1186.9
MG100	1192.1
MD100	1193.5
GA50-MG50	1189.5
GA50-MD50	1190.2
MG50-MD50	1192.8
GA33-MG33-MD33	1190.8
GA66-MG17-MD17	1183.7
GA17-MG66-MD17	1189.8
GA17-MG17-MD66	1192.1

GA = gum arabic, MG = mesquite gum, MD = maltodextrin DE 10.

2.5. Drop shrinkage

Báez-González (2002) determined the drop volume shrinkage (V_{sh}) of 40% (w/w) aqueous solutions of GA, MG and MD as a function of moisture content (X) dried isothermally under the conditions mentioned in Section 2.4 by triplicate. In short the procedure used was as follows: (1) a drop of a biopolymer 40% (w/w) aqueous solution was put on a glass slide; (2) micrographs of the $X-Y$, $X-Z$ and $Y-Z$ planes of the drop (that exhibited an ellipsoid shape) were taken; (3) the area of each plane was calculated with an Image Analysis System software; (4) with these areas the volume of an ellipsoid was calculated and approximated to that of a sphere; (5) steps 1–4 were repeated as the drops were dried isothermally at intervals of approximately 10% moisture content decrease (determined by drop mass loss); (6) V_{sh} is obtained by plotting the ratio of V (the drop volume at a given moisture content) to V_0 (the initial drop volume) against moisture content. The experimental points are then fitted with a polynomial. The polynomial describing V_{sh} was:

$$V_{sh} = \frac{V(X)}{V_0} = A + BX + CX^2 \quad (1)$$

2.6. Effective diffusivity

The effective diffusivity coefficients (D_{eff}) considering shrinkage and moisture dependence were determined according the method proposed by Raghavan, Tulasidas, Sablani, and Ramaswamy (1995), applying an approximate analytical solution for Fick's second law to an isotropic spherical geometry and considering a constant moisture surface concentration (Crank, 1975) given by:

$$M = \frac{X - X_e}{X_0 - X_e} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left[-n^2\pi^2 D_{eff}\frac{t}{[R(X)]^2}\right] \quad (2)$$

where M is the moisture ratio [dimensionless], X the moisture content at time t [kg H_2O/kg d.s.], X_0 and X_e are

the initial and equilibrium moisture content [kg H_2O/kg d.s.], respectively, and $R(X)$ is the radius of the biopolymer drop expressed as a function of moisture content [m].

The procedure followed is summarized below:

1. Obtain experimentally the isothermal drying curves at different temperatures.
2. Determine the experimental moisture ratio (M_{exp}).
3. Determine:

$$R(X) = V_{sh}^{1/3} R_0 \tag{3}$$

where R_0 is the initial radius of the biopolymer drop

4. Substitute Eq. (3) in Eq. (2).
5. Assume a value of D_{eff} using the first 50 terms in Eq. (2) to calculate M.
6. Compare M_{exp} with M and if:
   $|M - M_{exp}| > 1 \times 10^{-10}$ return to step 4, and assume a new D_{eff}
   $|M - M_{exp}| < 1 \times 10^{-10}$ end computation, and consider the latest assumed value as that of D_{eff}.

2.7. Activation energy

The activation energy (E_a) was determined calculating a D_{eff} for each biopolymer blend, which in turn is temperature dependent following an Arrhenius-type relationship.

The procedure followed for determining E_a was as follows:

1. Obtain for each biopolymer treatment a plot X versus D_{eff} for each isothermal drying temperature.
2. Determine for each biopolymer treatment an average effective diffusivity ($\overline{D_{eff}}$) within the experimental temperature range with the following equation:

$$\overline{D_{eff}} = \frac{\int_{X_0}^{X_1} D_{eff}(X)\mathrm{d}X}{\int_{X_0}^{X_1} \mathrm{d}X} \tag{4}$$

where X_1 is the final moisture content achieved after the drying process [kg H_2O/kg d.s.], and $D_{eff}(X)$ is the effective diffusivity at a specific moisture content [m^2/s].

3. Using the following Arrhenius-type relationship:

$$\overline{D_{eff}} = D_0 \exp\left[-\frac{E_a}{RT}\right] \tag{5}$$

a plot of $\ln \overline{D_{eff}}$ versus $1/T$, yields a straight line with slope $-E_a/R$, where $\overline{D_{eff}}$ is in [m^2/s], D_0 is the Arrhenius factor [m^2/s], E_a is in [kJ/mol], R is the gas constant (8.314×10^{-3} kJ/mol K), and T is the absolute temperature (K).

3. Results and discussion

3.1. Density

The data of the initial density of the different 40% weight biopolymer aqueous solution treatments are given in Table 2.

3.2. Drop shrinkage

The drop volume shrinkage for the biopolymers blends (V_{shb}) was estimated from the polynomials describing V_{sh} for GA, MG and MD (Báez-González, 2002), assuming that the component volumes of each biopolymer in the blend are additive, leading to the simple averaging formula:

$$\frac{1}{V_{shb}} = \sum_{i=1}^{n} \frac{x_i}{V_{shi}} \tag{6}$$

where n is the number of components in the blend, V_{shi} is the drop volume shrinkage of the ith component, and x_i is the mass fraction of this component. The polynomial coefficients A, B and C for the biopolymer blends of Table 1 are given in Table 3.

3.3. Effective diffusivity

A plot of moisture content against effective diffusivity for selected biopolymer blends GA100, MG100, MD100, GA66-MG17-MD17 and GA17-MG66-MD17 at 60 °C is shown in Fig. 2. All of the curves exhibited non-linear behavior characterized by three main regions: (1) a high moisture content region (~1.5–1.0 kg H_2O/kg d.s.), where the effective diffusivity coefficients have low values due to a 'settling down' period at the beginning of the drying process (Brennan, Butters, Cowell, & Lilly, 1976) in which the surface of the forming biopolymer film establishes equilibrium with the drying air; (2) an intermediate moisture content region (~1.0–0.4 kg H_2O/kg d.s.), in which the effective diffusivity remains practically constant and exhibits its highest values. During this period the surface of the biopolymer film is saturated with liquid water, which

Table 3
Coefficients of polynomial model describing biopolymer drop shrinkage

Biopolymer blend code	A	B	C
GA100	0.6867	0.4469	−0.1608
MG100	0.6565	0.0063	0.1411
MD100	0.5844	0.2125	0.0572
GA50-MG50	0.6716	0.2266	−0.0099
GA50-MD50	0.6355	0.3297	−0.0518
MG50-MD50	0.6204	0.1094	0.0992
GA33-MG33-MD33	0.6361	0.2197	0.0124
GA66-MG17-MD17	0.6642	0.3322	−0.0724
GA17-MG66-MD17	0.6494	0.1163	0.0755
GA17-MG17-MD66	0.6140	0.2173	0.0344

GA = gum arabic, MG = mesquite gum, MD = maltodextrin DE 10.

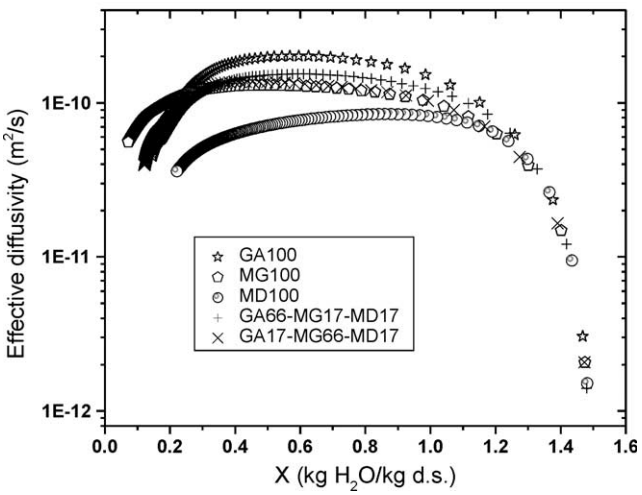

Fig. 2. Influence of moisture content on effective diffusivity of selected biopolymer blends at 60 °C.

is associated to the constant drying rate; and (3) a low moisture content region (~0.4–0.05 kg H_2O/kg d.s.) in which the effective diffusivity decreases with decreasing moisture content. This period is associated to the falling drying rate and is that in which the shrinkage of the biopolymer drop reaches its maximum.

Fig. 3. depicts the same behavior as in Fig. 2 for blend GA66-MG17-MD17, at the three isothermal drying temperatures of 50, 60 and 80 °C. It is clearly observed that the values of the effective diffusivity increase with increasing temperature when the moisture content is below approximately 1.3 kg H_2O/kg d.s., however, above this moisture level there is no temperature dependence of diffusivity, signifying that the activation energy at this high moisture is zero. The rest of the biopolymer treatments showed the same trend as that of blend GA66-MG17-MD17. These high moisture content levels correspond to the initial stage of the drying process in which an energetically unhindered free

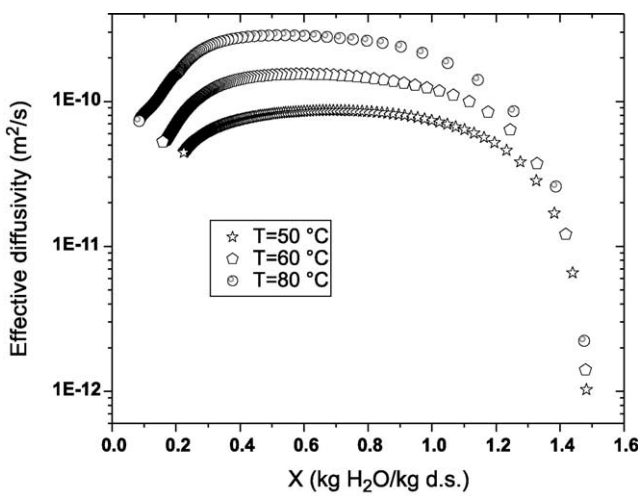

Fig. 3. Influence of moisture content and temperature on effective diffusivity of biopolymer blend GA66-MG17-MD17.

moisture evaporation takes place. It is also at this initial stage when the formation of the two-dimensional, dense skins takes place. For this reason the calculation of D_{eff} should include the overall process from room temperature to the isothermal temperature as well as the drying of the biopolymer blends. Báez-González, Pérez-Alonso, Beristain, Vernon-Carter, and Vizcarra-Mendoza (2003) calculated D_{eff} of the same pure GA, MG and MD aqueous solutions used in this work employing Regular Regime Theory, which considers a falling rate period only when the rate of drying is governed by diffusion processes. D_{eff} calculated by both methods for the three biopolymers were of the same order and very close in numerical value.

Fig. 4 shows a comparison of the experimental and calculated data of the moisture ratio as a function of drying time for biopolymer blend GA17-MG66-MD17 at 60 °C, both with and without drop shrinkage. It is clear from Fig. 4 that the calculated data which consider drop shrinkage overlap the experimental data, whereas the calculated data which does not consider shrinkage show considerable deviation from the experimental data.

The effect of temperature on the average effective diffusivity adequately fitted the Arrhenius-type correlation with r values above -0.90 for all the blends (Table 4). Selected plots of $\ln \overline{D}_{eff}$ versus $1/T$ are shown in Fig. 5 and the average activation energies for all of the biopolymer blends are shown in Table 4. A comparison of E_a for the three pure biopolymers indicates that maltodextrin had the highest E_a (30.2070 kJ/mol), followed by mesquite gum (E_a = 24.5263 kJ/mol) and gum arabic (E_a = 18.0778 kJ/mol), pinpointing that the first may be considered as the most suitable of the three wall materials for providing protection against oxidation to spray-dried encapsulated lipids. There is ample evidence corroborating the suitability of maltodextrin for protecting carotenes against degradation by oxidation (Desobry, Netto, & Labuza, 1999; Wagner &

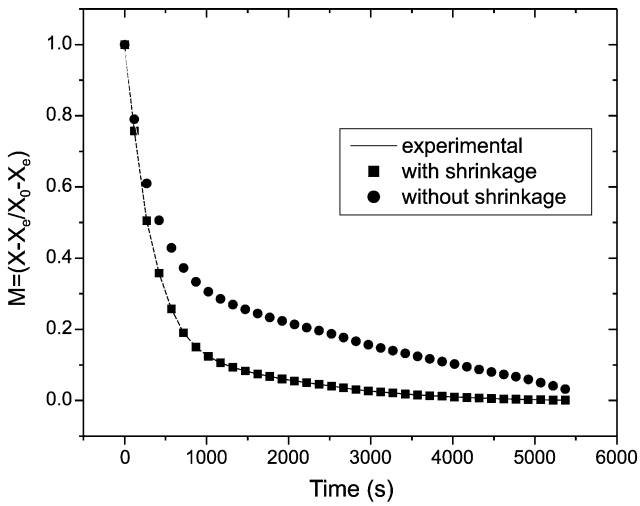

Fig. 4. Comparison between the experimental and the calculated dimensionless moisture content with and without shrinkage of biopolymer blend GA17-MG66-MD17 at 60 °C.

Table 4
Activation energies of biopolymers blends

Biopolymer blend code	E_a (kJ/mol)	r	SD
GA100	18.1	−0.95	0.01
MG100	24.5	−0.99	0.04
MD100	30.2	−0.98	0.11
GA50-MG50	19.6	−0.99	0.03
GA50-MD50	25.3	−0.99	0.07
MG50-MD50	25.7	−0.99	0.07
GA33-MG33-MD33	27.6	−0.90	0.30
GA66-MG17-MD17	33.5	−0.99	0.11
GA17-MG66-MD17	30.6	−1.00	0.00
GA17-MG17-MD66	19.9	−0.94	0.16

GA = gum arabic, MG = mesquite gum, MD = maltodextrin DE 10.

Warthesen, 1995). However, maltodextrins do not possess emulsifying properties (King, 1995), so that overall they are poor microencapsulating agents when used on their own, as they exhibit low oil retentions (Sankarikutty et al., 1988). On the other hand, both gum arabic (gum acacia) and mesquite gum are considered very effective emulsifiers, rendering microcapsules with high oil retentions (in the range of 80–93% of starting oil) (Beristain, García, & Vernon-Carter, 2001; Beristain & Vernon-Carter, 1994, 1995; Sankarikutty et al., 1988). Furthermore MG has been reported as offering a good protection against oxidation to orange peel oil stored in environments with water activities as high as 0.628 (Beristain, Azuara, & Vernon-Carter, 2002). It can be observed in Table 4 that biopolymers blends containing a large proportion of gum arabic (GA66-MG17-MD17) or of mesquite gum (GA66-MG17-MD17) exhibited slightly higher activation energies than treatment MD100, so that presumably these blends provide a superior protection against oxidative processes to the encapsulated lipids than pure MD, have lower costs than pure GA, and are likely to achieve equivalent emulsifying capacities and oil retention as GA and MG as suggested in microencapsulation studies utilizing blends of these materials (Beristain et al., 1999; Beristain & Vernon-Carter, 1995; Sankarikutty et al., 1988; Thevenet, 1995).

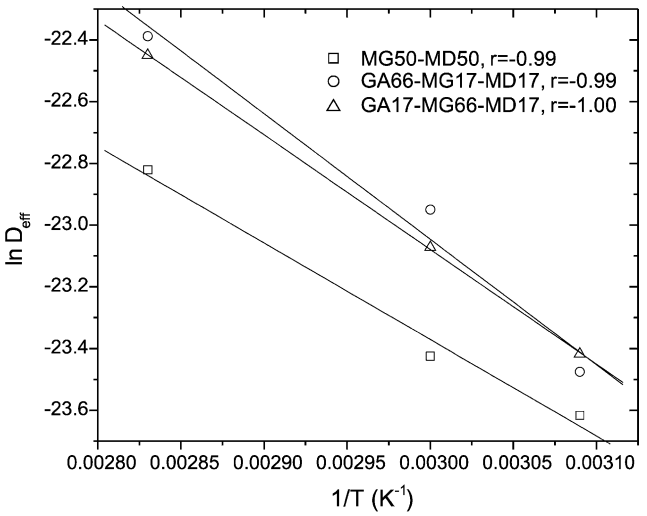

Fig. 5. Arrhenius-type temperature dependence of the average moisture diffusivity of selected biopolymer blends.

4. Conclusions

Estimation of the activation energy of carbohydrate polymers blends provides a quantitative discriminating parameter for selecting the most suitable materials for protecting microencapsulated lipids against oxidative deterioration. Consideration of drop volume shrinkage is of the utmost importance for obtaining reliable activation energy values. The assumption that drop volume shrinkage of the blends can be described by the additive volumes of the individual polymers making up the mixture is validated by the overlapping of the experimental data and the calculated data considering shrinkage of the moisture ratio. The difficulty in using this method is determining experimentally the drop volume shrinkage of every conceivable blend. However, if a data bank of the polynomial models describing the drop shrinkage of say the 10 or 15 most used or potentially employable wall materials is gathered, then by drying isothermally any particular blend in a TGA and estimating the drop volume shrinkage of the blend, its activation energy can be reliably estimated.

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