

Rate of fatty acid transport in glassy biopolymers: A free volume based predictive approach



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ABSTRACT

Metastable properties of biopolymer networks affect significantly the diffusion kinetics of bioactive compounds. That was shown to be the case in high solid samples of protein and polysaccharide supporting a homogeneous distribution of polyunsaturated fatty acids. Thermomechanical behaviour of these matrices was characterised in relation to their glass transition temperature (T_g). A free volume theory of diffusion was considered to treat transport phenomena of fatty acids within glassy polymers. It was found that at $T > T_g$ the effective diffusion coefficient of microconstituent transport would increase in accordance with the free volume of the polymer matrix. Fitting experimental diffusivity data in glassy polymers to a free volume based theory generates a two-parameter equation that calculates the extent of molecular interaction between macromolecule and microconstituent. Gradual substitution of polymer with small-molecule co-solute, glucose syrup in this case, induces a plasticising effect that profoundly affects the level of interaction, hence the diffusion of fatty acids in the condensed biomaterial.

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This article has been written in celebration of the scientific work of Professor Glyn O. Phillips on the occasion of his 90th birthday in 2017. He is a Founding Father of research in structure-function relationships of industrial hydrocolloids and Founder of the prestigious journal *Food Hydrocolloids*. We wish him many happy returns in leading the field of hydrocolloid research.

In the area of high-solid systems, biopolymer mobility at the vicinity of the glass transition temperature is related to complex molecular phenomena. Within the glass transition region, amorphous viscoelastic materials see a dramatic reduction in free volume with rapid cooling, which can be monitored as a broad variation in heat capacity or steady shear viscosity (Perez, 1990; Roudaut & Champion, 2011). The dramatic decrease in viscosity is accompanied by reduced thermal vibration leading to limited translational mobility that promotes physicochemical stability (Le Meste, Champion, Roudaut, Blond, & Simatos, 2002; Roudaut, Maglione, van Dusschoten, & Le Meste, 1990). Devitrification can be achieved by increasing the temperature above T_g , with the frozen-in molecules starting to resonate leading to a structural relaxation of the condensed matrix (Roudaut, Simatos, Champion, COUNTERAS-LOPEZ, & Le Meste, 2004).

Mechanical properties of the polymeric material within the glass transition region can be followed with the free volume theory, as quantified by the Williams-Landel-Ferry (WLF) equation (Ferry, 1991; Kasapis, 2009, pp. 225–260). The approach is followed presently for several matrices based on natural polymers, i.e. high methoxy pectin/glucose syrup, κ -carrageenan/polydextrose, and whey protein/glucose syrup at various combinations: 100:0, 80:20, 70:30, 60:40, 40:60 and 0:100 (w/w).

We prepared polysaccharide matrices that were composed of 3% (w/w) high-methoxy pectin (HMP) with 81% (w/w) glucose syrup and 2% (w/w) κ -carrageenan with 83% (w/w) polydextrose. To each formulation, 1% (w/w) of fatty acid, i.e. oleic acid and α -linolenic acid were added, respectively. Polysaccharide powder was dissolved in Milli-Q water at about 90 °C, followed by cooling to 50 °C for the addition of co-solute. Temperature was decreased even further to 40 °C prior to fatty acid addition. A 2 M HCl solution was added to the HMP/glucose syrup mixture to obtain pH 3, which is needed for gelation, and 50 mM KCl solution was utilised for gelation of the κ -carrageenan/polydextrose sample. These were concentrated under vacuum to achieve 85% (w/w) total solids.

Whey protein/glucose syrup (wp/gS) matrices were prepared by dissolving whey protein isolate at ambient temperature for 2 h in Milli-Q water, diluting the glucose syrup solution in Milli-Q water and mixing them up at appropriate levels to create a system of 30% total solids. That was stirred for 15 min prior to addition of 1% (w/

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relaxation of the polymeric matrix.

The study was further advanced by seeking to understand the release mode of fatty acid using the generalised Fickian law according to the empirical equation of Peppas and Peppas (1994). This calculates values of the diffusion exponent (n), which are reproduced for all systems in Table 1. Results suggest that the diffusion of fatty acids in polysaccharide is Less Fickian ($n < 0.5$) due to the incongruous chemical nature of the two components, whereas the partially hydrophobic nature of whey protein accelerates permeability of the microconstituent leading to a more Fickian (anomalous) transport ($n > 0.5$).

The consistency in experimental observations allowed us to select the “half time” Fickian equation in order to estimate the effective diffusion coefficient (Ritger & Peppas, 1987; Wang, Wu, & Lin, 2008):

$$\frac{M_{\infty} - M_t}{M_{\infty} - M_i} = 4 \left(\frac{D_{eff} t}{\pi L^2} \right)^{1/2} \quad (5)$$

where, $(M_{\infty} - M_t)/(M_{\infty} - M_i)$ is the cumulative amount of fatty acid release at various timeframes of experimentation, t presents the experimental time intervals, L is the thickness of the delivery vehicle (slab) and D_{eff} is the effective diffusion coefficient of fatty acid. The latter can be affected by several factors including temperature, presence of plasticisers, concentration and nature of the polymeric material, penetrant and degree of crosslinking (Brandelero, Yamashita, & Grossmann, 2010; George & Thomas, 2001).

Diffusion coefficient values are reproduced at -16°C in Table 1, i.e. a temperature regime where our systems are in a variable state of vitrification. The plasticising influence of small molecule co-solute, in relation to the diffusivity of fatty acid, is demonstrated once more in the proteinaceous matrices. Thus, higher values of D_{eff} from 1.63 to $2.50 \times 10^{-10} \text{ m}^2/\text{s}$ are obtained with the addition of glucose syrup in the whey protein network. Similar results were found in a study of gas permeability in edible films made with changing amounts of sugar and moisture (Arvanitoyannis, Psomiadou, & Nakayama, 1996).

Some experimental observations of free volume and effective diffusion coefficient for our whey protein/glucose syrup samples obtained from equations (1)–(5) are depicted in Fig. 1. Clearly, there is a congruent increase in the values of both concepts with higher temperatures of observation above T_g . This qualitative agreement

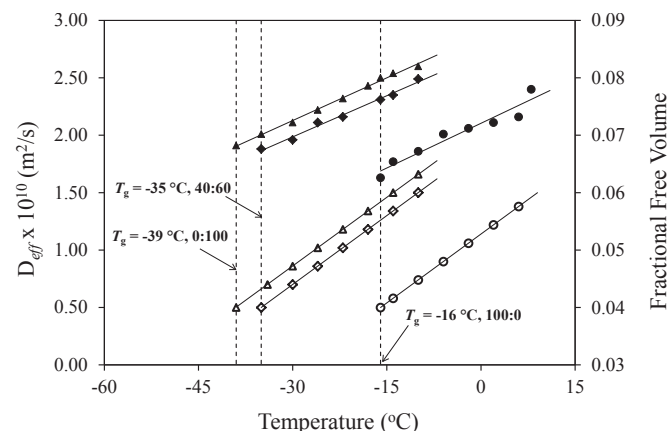


Fig. 1. Diffusion coefficients (D_{eff}) of 1% linoleic acid through 79% whey protein/glucose syrup matrices at 100:0 (circle), 40:60 (diamond) and 0:100 (triangle) presented as closed symbols (left y-axis), and fractional free volume of the condensed matrix within the glass transition region presented as opened symbols (right y-axis).

between macro- and micromolecular processes argues that the free volume theory of diffusion might be a unifying concept for both molecular phenomena (Beichel et al., 2013; Cohen & Turnbull, 1959; Doolittle, 1951; Fujita, 1991; Vrentas & Duda, 1979). In order to encompass the molecular mobility of both dispersant and monolithic matrix, a shift factor of diffusion can be utilised in the form: $-\log a_T = \log [D(T)/D(T_g)]$ (Karbowski et al., 2011; Lohfink & Silescu, 1993). Inclusion of the diffusion shift factor in the framework of equations (1)–(5) generates the following mathematical expression (Panyoyai & Kasapis, 2016):

$$\log \left[\frac{D_{eff}(T)}{D_{eff}(T_g)} \right] = \frac{\xi}{2.303} \left[\frac{1}{f_g} - \frac{1}{f} \right] \quad (6)$$

which unveils a linear relationship between effective diffusion coefficient and inverse of fractional free volume. Parameter ξ is the critical molecular volume of the jumping unit of fatty acid (v_s^*) to that of the biopolymer matrix (v_m^*), often written as $\xi = v_s^*/v_m^*$ (Costa & Storti, 2010; Ehlich & Silescu, 1990).

Fig. 2 demonstrates this linearity for polymer/co-solute mixtures extending from pure whey protein to glucose syrup preparations. Good linear fits are obtained between effective diffusion coefficient and inverse fractional free volume ($r^2 = 0.97 \pm 0.02$) for all systems tested, which leads to a credible estimation of parameter ξ . In brief, the term jumping unit refers to the availability of “holes” or vacant space within the system allowing interstitial mobility (Danner, 2014; Fujita, 1991). In concentrated systems, molecules migrate by jumping from one void to another, and this is affected by the redistribution of free volume as a result of changes in temperature.

There are two criteria that have to be fulfilled for molecules to migrate: first, there is sufficient space to accommodate the size of diffusing species and second, these should possess enough energy to overcome attractive forces and move to the neighbouring voids (Barrer, 1957; Zhang & Wang, 1987b). When the molar volume of the jumping unit of the system is much higher than the molar volume of the diffusant ($v_s^* \ll v_m^*$), creating a low mesh-size network, the diffusant can only move following segmental rearrangements of the polymeric network from its state of dynamic equilibrium (Ehlich & Silescu, 1990; Roussanova, Andrieux, Alam, & Ubbink, 2014).

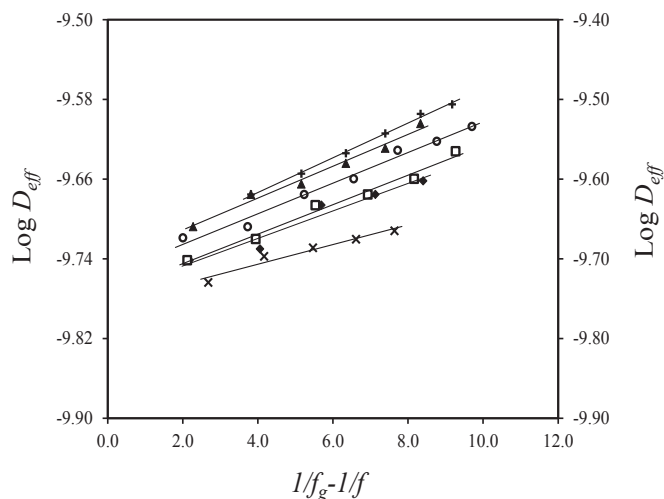


Fig. 2. Diffusion coefficients (D_{eff}) versus inverse function of fractional free volume of linoleic acid release from whey protein/glucose syrup matrices at 100:0 (X), 80:20 (◆), 70:30 (□), 60:40 (○), 40:60 (▲) and 0:100 (+).

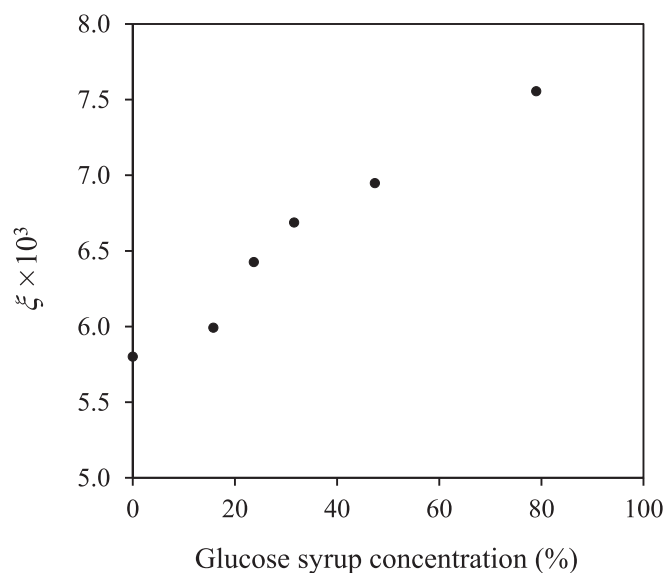


Fig. 3. Coupling parameters (ξ) of linoleic acid release from whey protein/glucose syrup matrices as a function of co-solute concentration (%).

Calculation of ξ values from Fig. 2 and equation (6) has been implemented for the polysaccharide and whey protein networks with glucose syrup or polydextrose, with outcomes being given in Table 1. These range from 4.25 to 7.55×10^{-3} and are in the same ballpark with earlier estimates on vitamin diffusion from condensed networks of natural polymers (Panyoyai & Kasapis, 2016). Moreover, these values have been plotted in Fig. 3 for the proteinaceous materials with increasing additions of co-solute.

In essence, they constitute evidence of the extent of interaction between the two constituents in the mixture and increase in an exponential fashion. This is due to the reduction in the critical molecular volume of the jumping unit of the polymer with the introduction of the low molecular weight co-solute (glucose syrup), with the critical molecular volume of linoleic acid remaining unaltered. Rapid redistribution of “hole-free volume” within the system facilitates jumping of fatty acids from one lattice point to another thus accelerating diffusion.

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