Translational Diffusion Coefficients of Volatile Compounds in Various Aqueous Solutions at Low and Subzero Temperatures

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Translational diffusion coefficients (D_{12}) of volatile compounds were measured in model media with the profile concentration method. The influence of sample temperature (from 25 to −10 °C) was studied on translational diffusion in sucrose or maltodextrin solutions at various concentrations. Results show that diffusivity of volatile compounds in sucrose solutions is controlled by temperature, molecule size, and the viscosity of the liquid phase as expected with the Stokes−Einstein equation; moreover, physicochemical interactions between volatile compounds and the medium are determinant for diffusion estimation. At negative temperature, the winding path induced by an ice crystal content of >70% lowered volatile compound diffusion. On the contrary, no influence on translational diffusion coefficients was observed for lower ice content.

INTRODUCTION

Aroma and texture are among the most important sensory characteristics of food products. The release of volatile compounds from the media is responsible for flavor perception. Flavor release depends mainly on two phenomena: volatility from the matrix (partition coefficient air/matrix) and molecular mobility (translational diffusion and mass transfer through phases). Moreover, the food matrix structure also influences aroma release and food texture. Furthermore, physical parameters such as temperature and viscosity influence both flavor release and food structure. Indeed, viscosity is of main importance to better understand and to predict flavor release from food as a function of temperature, particularly at low and subzero ones. The phase transition in a product from glass to rubber, for instance, induces an increase in molecular mobility of matrix molecules (*1*). Moreover, the molecular mobility of small molecules in food may govern the stability of frozen products in the case of diffusion-controlled reaction (*2*, *3*). Thus, gaining access to translational diffusion coefficients may yield very useful information. The data, however, are scarce, especially for the temperature domain below 0 °C. NMR determinations of translational diffusion coefficients are reported at temperatures down to −15 °C using a pulsed field gradient spin−echo method (*4*), but this experiment seems nonadaptable for the diffusion of volatile compounds, which are often at low concentration, in the parts per million range. Therefore, our first objective was to develop a method to measure translational diffusion coefficients of volatile compounds that can be used at negative temperatures. Given the paucity of diffusion data at temperatures below 0 °C, it has been proposed to test prediction relationships (*5*−*7*). Diffusion of a spherical molecule, 1, in a solvent, 2 (or a dilute solution) (D_{12} or D_{th}), had been related to the hydrodynamic radius of the spherical diffusing molecule, r_1 (in m), temperature (*T* in K), and viscosity, η_2 (in Pa.s) of the medium 2, with the Stokes−Einstein equation (eq 1):

$$D_{12} = D_{th} = \frac{kT}{6\pi r_1 \eta_2} \qquad (1)$$

where *k* is the Boltzmann constant (1.3805×10^{-23} J K^{-1}). This equation is applied when solute molecules are greater than solvent molecules. Although this relationship was derived for a very special situation, many authors have used it as a starting point in developing correlations (*8*). Interactions between diffusing molecules and the medium have been previously introduced by Kowert and Kivelson in 1976 (*9*). These authors introduced a coupling constant (κ) in the Debye−Stokes−Einstein relationship to quantify these interactions as described by the relationship

$$D_{12}^* = \frac{kT}{6\pi r_1 \eta_2 \kappa} \qquad (2)$$

κ represents globally the number and/or the force of the interactions between the diffusing molecules and the media; interactions can be of two kinds: "stick" or "slip". The first one shows strong interactions with the media, whereas the second one presents no interaction (*9*). According to eqs 1 and 2, the coupling constant (κ) is the quotient of the theoretical value of diffusion coefficient (D_{12}) and the experimental diffusion coefficients (D_{12}^*).

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Several studies (*10, 11*) had shown that for acetone, in aqueous poly(ethylene glycol) solutions and sucrose solutions, the diffusivity decreases with the decrease of water content. Voilley and Bettenfeld (*11*) investigated the influence of water activity on aroma translational diffusion in gels with glucose syrup DE 61.5 of different water activity values. Translational diffusion coefficients decreased greatly for small decreases in A_w (0.14 unit) at high A_w values. Furthermore, these authors showed that there was no influence of 1% agar addition in the media on aroma translational diffusion. On the contrary, high polysaccharide concentrations in the media ($\sim$10%) can affect translational diffusion because they may induce phase separation or because of their important intrinsic viscosity (*12*). Volatile molecule diffusivity in concentrated solutions was found to decrease when the molecular weight of the molecule increased (*10*). Moreover, the diffusivity of solutes such as fluorescein (*12, 13*) decreased as the solid matter content increased for sucrose solutions or sucrose polysaccharide mixtures. However, no data had been reported in the literature dealing with aroma diffusion at low and subzero temperatures. Furthermore, the ice crystal effect on the diffusion of small molecules was scarcely studied. The importance of the latter is to better understand aroma release at subzero temperatures and the influence of ice on volatile compound diffusion, which determine the sensory characteristics of frozen food such as ice creams. Therefore, this research dealt with the measurement of translational diffusion coefficients of flavor compounds in food models. The effect of both temperature and media composition was studied on various aqueous solutions at temperatures from 25 to −10 °C. Moreover, the determination of the main physical−chemical parameters, which control the translational diffusion coefficients in frozen systems, is the first objective of this work in order to predict small molecule diffusion without measurement. These findings should allow a better understanding of the flavor stability of frozen foodstuffs during industry processes and/or storage.

MATERIALS AND METHODS

Material. *Volatile Compounds.* Two homologous series of different chemical families were selected: methyl ketones (from C$_3$ to C$_8$: acetone, 2-butanone, 2-hexanone, and 2-octanone) and ethyl esters (from C$_4$ to C$_8$: ethyl acetate, ethyl butanoate, and ethyl hexanoate); *n*-hexanol was also included to compare volatile compounds with the same carbon atom number. All of the volatile compounds were supplied by Aldrich-Sigma Co. (Steinheim, Germany) with a minimum purity of 98%.

Model Media. Diffusion media consisted of 1% (w/w) agar gel with water and aqueous solutions of sucrose or maltodextrin. Sucrose (Prolabo) at concentrations from 15 to 57.5% and maltodextrin (MD) at a concentration of 57.5% (Roquette, Lestrem, France) with two dextrose equivalents (DE) (21 and 47) were selected as cosolute in order to study the substrate molecular weight effect.

Methods. *Preparation of the Model Media.* To study aroma diffusion in water, gelled media allowed aroma diffusivity in immobilized water. The presence of 1% (w/w) of agar (Biokar Diagnostics, Beauvais, France) in the media does not interact with volatile compounds (*11, 14*). A given amount of water was heated to 70 °C. Then, 1 g of agar was added into the hot water; after 15 min of stirring, a given amount of substrate (according to **Table 2**) was added and stirred for 10 min more at the same temperature. The water loss by heating was eventually corrected with adding water. Finally, glass test tubes of 10 cm height and 0.5 cm diameter were filled with the liquid agar solution. The test tubes were placed at room temperature in order to let the agar solidify. Then, in the case of the media studied at subzero temperatures, the glass tubes were stored at −30 °C in a freezer. After 24 h, the gel tubes were stored at the temperature of analysis (−5 or −10 °C).

Diffusion Measurement. The translational diffusion coefficient of the volatile compounds was measured using the profile concentration method, which is an accurate technique to determine translational diffusion coefficients (*11, 14*). Pure volatile compound was put in the bottom of an airtight glass jar. Then, the gel tubes were introduced into the glass jar. To prevent gel dehydration, 4−5 mL of the same substrate solution (sucrose or maltodextrin) was poured into the glass jar. A fan was placed on the top of the jar to maintain a homogeneous aroma atmosphere. The jar was stored in a temperature-controlled chamber at the temperature of analysis (25, 4, −5, and −10 °C). After a given time depending on experiment temperature, the glass test tube was sampled and then cut into slices of $\sim$2 mm each. Every slice was put in a vial containing water; to quantify the aroma concentration in each slice, 1 μL of each flask liquid was analyzed by gas chromatography (GC).

The translational diffusion coefficients (*D*) were calculated from experimental values, by a solution of Fick's second law, for diffusion in a semi-infinite medium (*15*) (eq 5)

$$\frac{C_{(x,t)}}{C_0} = \frac{1}{2}\text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{3}$$

where $C_{x,t}$ is the solute concentration at a distance x (m) after a time t (s), C_0 is the constant concentration of the diffusing compound in the saturated atmosphere ($x = 0$), D is the apparent diffusion coefficient (m^2 s^{-1}), and erfc is the complement of the error function (erfc = 1 − erf).

Gas Chromatography Analysis. A Chrompack CP-9000 GLC with a flame ionization detector (FID) was used to quantify the aroma amount in the aqueous phase. The GLC was coupled to a Shimadzu C-R6A Chromatopac integrator. Flavor compounds were separated in a stainless steel packed column of 3 m length and 2.2 mm internal diameter; the stationary phase was a 10% Carbowax 20M, W-AW 100−120 mesh. The analysis conditions were as follows: oven temperature, 70 or 120 °C isotherm; FID temperature, 200 °C; injector temperature, 190 °C. The gas flow rates were as follows: nitrogen (carrier gas), 20 mL min^{-1}; hydrogen, 25 mL min^{-1}; and air, 250 mL min^{-1}. Pure volatile compounds were used as internal standard.

Statistical Analysis. Statistical analysis of the different replicates was carried out using the statistical analysis system SAS (SAS Institute, Inc., Cary, NC) (*16*). A variance analysis and a mean comparison by a Student−Newman−Keuls test were done with a 95% confidence level.

RESULTS AND DISCUSSION

From an experimental point of view, the adapted setup to measure translational diffusion coefficients of volatile compounds at negative temperatures allowed measurements with relatively low variation coefficients, but it showed some limits. Some steps in diffusion experiments are critical, such as when the gel is cut into slices and the size of the gel slices (2 mm). Volatile compound concentration in the first agar slice could also vary, resulting in a variation of C_0 (eq 3). However, according to eq 3, only the ratio between the volatile compound concentration (*C*) in the different slide of the gel and the maximum concentration of the first slide (C_0) is important for diffusion coefficient determination. The time needed for aroma translational diffusion, in particular at subzero temperatures, is another critical parameter for this technique. On the one hand, the fastest diffusion coefficients were obtained within 20−24 h in water for acetone, 2-butanone, and ethyl acetate at 25 °C. The longest diffusion time obtained was up to 3 months for *n*-hexanol in a 57.5% sucrose or MD DE 21 at −10 °C.

Aroma Diffusion at 25 °C. The aroma translational diffusion coefficients were measured in water (immobilized by the agar gel) at 25 °C; results are given in **Table 1**. Diffusivity within a homologous series of volatile compounds in water is not significantly different according to the variation coefficient (30%). However, the higher the molecular weight and the molar volume are, the lower the mean diffusion coefficients are.

Translational Diffusion Coefficients of Volatile Compounds

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Table 1. Experimental and Literature Values of Flavor Compound Diffusion in Water at 25 °C

| aroma compound | diffusion coefficient $D \times 10^{10}$ m^2 s^{-1} | |
	exptl	lit.
acetone	14.27 ± 4.34	12.8^a
		12.7^b
		15.6^c
2-butanone	13.52 ± 3.44	
2-hexanone	11.82 ± 2.26	
2-octanone	10.06 ± 2.04	
ethyl acetate	16.16 ± 1.36	$(11.7)^b$
ethyl butanoate	9.96 ± 2.09	
n-hexanol	11.16 ± 1.97	$(5.6)^b$

[a] Hayduk and Laudie (*23*). [b] Voilley and Bettenfeld (*11*). [c] Johnson and Babb (*24*).
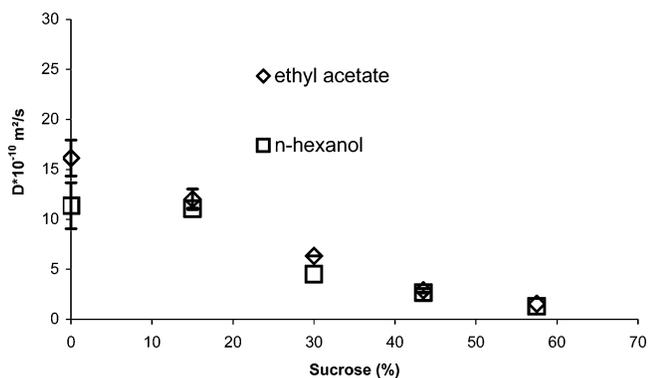
Figure 1. Translational diffusion coefficients of ethyl acetate and n-hexanol in aqueous sucrose solutions at 25 °C.

Through a homologous series such as ketones, diffusion decreases when the carbon chain length increases and thus with the hydrodynamic radius of the molecule. The same observation is made for the two esters, ethyl acetate and ethyl butyrate. When translational diffusion rates of compounds having six carbon atoms (C_6) are compared, diffusion decreases according to the chemical function in the following order: ketones > esters. A reverse order is obtained for compounds having four carbon atoms (C_4). Results of the flavor compound diffusion in water (1% agar gel) were compared with the few values available in the literature. Our results measured in water are in agreement with those from the literature (**Table 1**). The agar gel at a concentration of 1% does not interact with the volatile compounds studied and does not change significantly their translational diffusion coefficient, as Voilley and Bettenfeld (*11*) demonstrated.

The greatest translational diffusion coefficient in water is that of ethyl acetate, whereas one of the lowest is that of n-hexanol. Considering these two volatile compounds as a representation of the extreme cases, the diffusivity of both volatile compounds as a function of sucrose concentration in the aqueous solutions at 25 °C is shown in **Figure 1**. It is observed that as the sucrose concentration increases, the translational diffusion coefficients decrease. The greater the sucrose concentration, the lower the diffusion coefficient at 25, 4, and −5 °C; as well as temperature decreases, volatile molecule diffusivities decrease (**Figure 2**). In the same way, the diffusion of ethyl acetate in the MD DE 21 and MD DE 47 media decreases 50 and 120 times, respectively, from 25 to −10 °C; temperature decreases n-hexanol diffusion in the MD DE 21 and MD DE 47 media by factors of 17 and 76, respectively, from 25 to −10 °C (**Figure 3**). Maltodextrins do not contain the same size and percentage
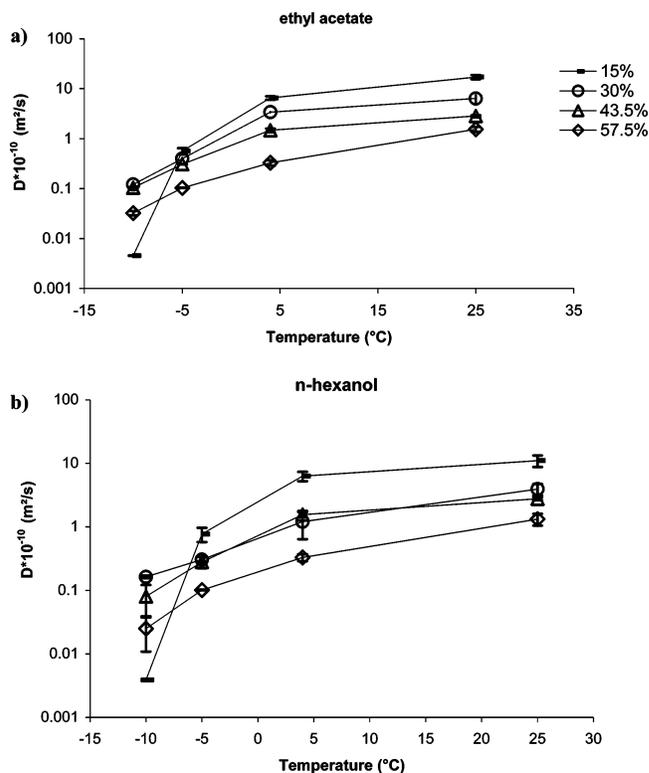
Figure 2. Translational diffusion coefficients of (**a**) ethyl acetate and (**b**) n-hexanol as a function of temperature in various aqueous sucrose solutions.
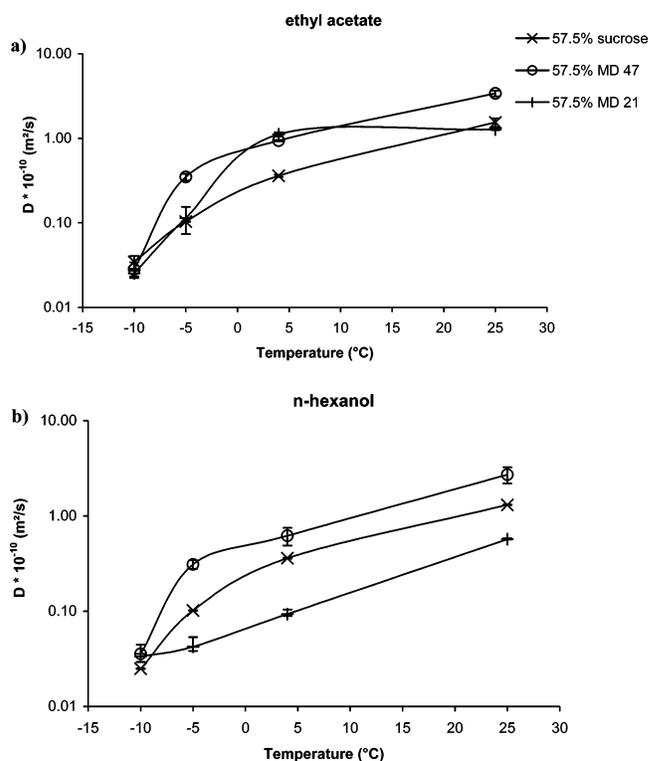
Figure 3. Translational diffusion coefficients of (**a**) ethyl acetate and (**b**) n-hexanol as a function of temperature in sucrose and maltodextrin (DE 47 and DE 21) solutions.

of glucose polymers; a mixture of larger glucose polymers is present in the MD DE 21 than in the MD DE 47. The heterogeneous composition of both of these polysaccharides could be the reason for diffusion coefficient differences at

Table 2. Composition of Frozen Solutions at −10 °C as a Function of Initial Concentration Calculated with Sucrose State Diagram (*17*)

% sucrose (w/w) at 20 °C	*T* (°C)	% sucrose (w/w) in the cryo-concentrated phase	% ice in the product	% cryocon-centrated phase in the product
15	−10	57.5	74	26
30		57.5	48	52
43.5		57.5	24	76
57.5		57.5	0	100

Table 3. Translational Diffusion Coefficients of Volatile Compounds in Aqueous Sucrose Solutions as a Function of Temperature ($p = 95\%$)

| | % sucrose in the media (w/w) | | | |
| | 15% | | 57.5% | |
T (°C)	ethyl acetate	*n*-hexanol	ethyl acetate	*n*-hexanol
25	1825 ± 225	1106 ± 230	154 ± 18	131 ± 3
−5	60.5 ± 8	77.25 ± 0.20	10.35 ± 1.00	10.2 ± 0.10
−10	0.457 ± 0.10	0.39 ± 0.001	3.46 ± 0.60	2.5 ± 0.14

subzero temperatures; the latter is more evident in the case of *n*-hexanol.

Influence of Ice Content on Aroma Diffusion. Substrate concentrations were chosen to study aroma translational diffusion in both diluted and concentrated sucrose solutions. To study the translational diffusion of volatile compounds in an isoconcentrated solution at both positive and negative temperatures, the initial concentration of substrate, that is, sucrose, was calculated according to the water−sucrose phase diagram (*17*). The concentration of the liquid remaining phase in a frozen product depends on the temperature below the temperature of ice freezing in the solution. Ice content can be calculated according to the cryoconcentration level: the difference between the initial concentration of the solution and the concentration of the liquid phase at a given temperature (this concentration is read on the state diagram). Thus, the ice content changes in each solution and depends on the initial sucrose content and temperature (**Table 2**). Hence, when working at − 10 °C, a 57.5% sucrose solution was obtained as liquid phase whatever the initial concentration of solution, so various ice contents in these solutions were a function of the initial concentrations. This allows one to study the tortuosity induced by ice crystals on aroma translational diffusion. At −10 °C, the ice contents in the 15, 30, 43.5, and 57.5% sucrose solutions were 74, 48, 24, and 0%, respectively. In **Table 3** the temperature effect on aroma diffusivity (ethyl acetate and *n*-hexanol) in aqueous sucrose solutions is displayed.

Translational diffusion coefficients of ethyl acetate and *n*-hexanol are plotted as a function of ice content for a 57.5% sucrose cryoconcentrated solution at −10 °C (**Figure 4**). When the ice content increased from 0 to almost 50%, the translational diffusion of volatile compound is not significantly different, which suggests that only the viscosity of the liquid phase seems to control diffusion. On the contrary, when ice content is higher (>70%), a significant decrease in volatile molecule diffusion is observed. For instance, *D* of ethyl acetate is highly decreased (400 times) in a 15% sucrose solution from 25 to −10 °C (which contains 74% ice). Therefore, for very high ice contents, it seems that ice may hinder aroma translational diffusion in an important way. Solid particles probably create a winding path, which increases the distance of diffusion at the molecular level.

Factors Governing Aroma Translational Diffusion in Concentrated Media. The viscosity of sucrose solutions is
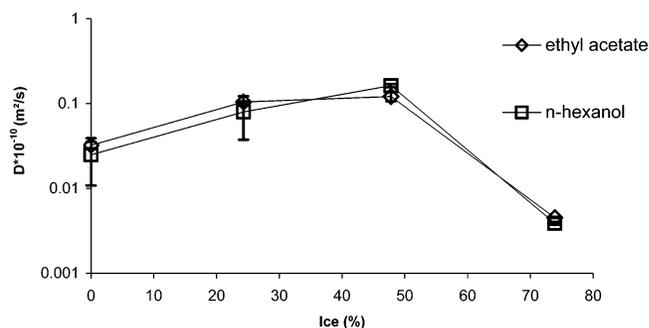
Figure 4. Translational diffusion coefficients of ethyl acetate and *n*-hexanol as a function of ice content for a 57.5% sucrose cryoconcentrated phase at −10 °C.

expected to increase when concentration increases and when temperature decreases (*13*, *18*) under both effects on temperature and cryoconcentration. The temperature effect on the translational diffusion coefficients of ethyl acetate and *n*-hexanol in a 57.5% sucrose solution from −10 to 25 °C was analyzed according to an Arrhenius plot. Moreover, the effect of a larger range of temperature was included in the same plot by adding literature values at positive temperatures of both volatile compounds in the same sucrose solution from 25 to 65 °C (*19*, *20*). It is observed that translational diffusion coefficients of both volatile compounds evolve as an Arrhenius function in the temperature range from 65 to −5 °C, and the activation energies of both volatile compounds are comparable (−43 and −41 kJ mol^{-1}, respectively). These values are in agreement with the activation energy of viscosity for the same solution (48 kJ mol^{-1}) given in the literature (*13*, *18*). Indeed, the viscosity of the solution, which translates the frictions between molecules, is a diffusion-governing parameter of translational diffusion as expected with the Stokes−Einstein equation (eq 1). However, viscosity may not be the only reference parameter to predict aroma diffusion. Hence, intermolecular interactions in the solution between volatile compounds and the media could strongly influence volatile compound diffusion.

Interactions between molecules can be evaluated from the diffusion coefficient with the calculation of the coupling constant between volatile compound and the diffusion media. In a first step, the hydrodynamic radius of ethyl acetate was determined with eq 2 using the experimental diffusion coefficient in water at 25 °C, considering that the coupling constant was equal to 1 in these conditions. In doing this calculation, the interactions in water−sucrose solutions were evaluated as a function of possible interactions in water; this sort of normalization with respect to interactions in water medium is done to calculate a hydrodynamic radius of the volatile compound extracted from diffusion data. It did not mean anything about the type of interactions in water. Then the calculated *r* value and the viscosity of 57.5% sucrose solutions from −10 to 25 °C were introduced in eq 1 to calculate a theoretical diffusion coefficient (D_{th}) as a function of temperature. The coupling constant κ was thus calculated by the quotient of the theoretical value of diffusion coefficient (D_{12}) and the experimental diffusion coefficients (D_{12}^*). The evolution as a function of temperature of the coupling constant κ of ethyl acetate in a 57.5% sucrose solution is shown in **Figure 5**. The κ values increase when temperature decreases, suggesting that the volatile compound diffusion showed weaker interactions with the diffusing media at −10 °C (slip conditions: κ value > 1) than at 25 °C, when the κ value tends to very low values (stick conditions).

Interactions between the diffusing molecules and the media can be also expressed with activity coefficient at infinite dilution

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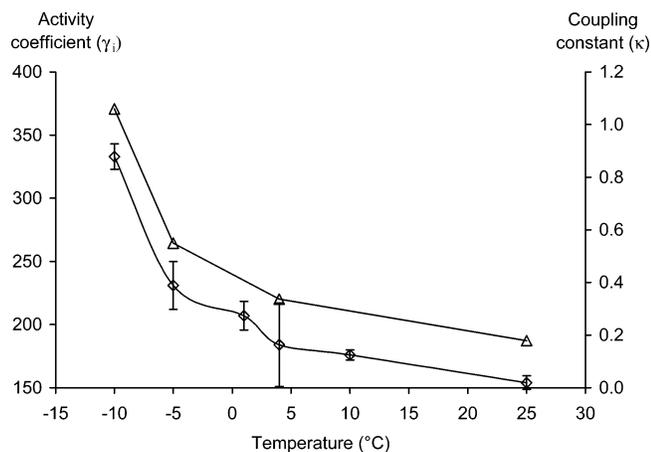
Figure 5. Influence of temperature on ($\diamond$) activity coefficient (γ_i^∞) (*21*) and (Δ) coupling constant (κ) of ethyl acetate in a 57.5% sucrose solution as a function of temperature.
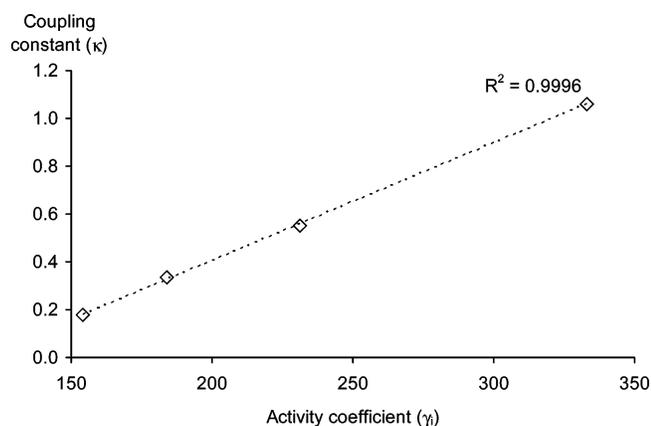
Figure 6. Correlation between the diffusion coupling constant (κ) and the activity coefficient (γ_i^∞) of ethyl acetate in a 57.5% sucrose solution.

(γ_i^∞). Some of the factors influencing this parameter are temperature and media characteristics such as sucrose concentration. The evolution of γ_i^∞ of ethyl acetate in 57.5% sucrose solutions with temperature is presented in **Figure 5**; γ_i^∞ was calculated from the measurement of the air−liquid partition coefficient of ethyl acetate in a 57.5% sucrose solution as a function of temperature (*21*). The activity coefficient γ_i^∞ represents the physicochemical interactions between a compound *i* and the media at a given temperature. It is observed that γ_i of ethyl acetate increases with temperature decrease (from 25 to −10 °C). The higher the γ_i^∞, the lower the interactions (strength and number) between ethyl acetate and the solution.

The diffusion coefficient and activity coefficient are known to be linked in diluted electrolyte solutions (*22*). Because κ and γ_i^∞ are parameters that quantify interactions between molecules, evolve in the same way (strong interactions = low κ = low γ_i^∞) and because these values were obtained with independent measurements (diffusion or partition coefficients), we compare them; the coupling constant κ is plotted as a function of γ_i^∞ in **Figure 6**. A highly correlated ($R^2 > 0.999$) linear dependence between both constants was obtained, which confirms the hypothesis about the physicochemical interactions influence on aroma diffusion in the temperature range studied. The same interactions seem to control both aroma volatility and diffusion. The correlation observed in a dilute system between activity coefficient and diffusion data seems to be also adapted for concentrated media.

Further research is needed to better understand aroma release with and without ice. Modeling of translational diffusion and aroma transfer can be carried out from the data generated in the present work. Moreover, it would be useful to study more complex matrices such as those containing lipids and proteins to better represent real systems.

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