Effect of Chemical Modification of Sodium Caseinate on Diffusivity of Aroma Compounds in Aqueous Solutions

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The concentration profiles obtained from a gel were used to measure diffusion of volatiles in water and in aqueous solutions of sodium caseinate glycosylated or not. The physicochemical interactions between solutes and substrates were studied by exponential dilution. As the aroma retention by sodium caseinate increased, the diffusion coefficient decreased. Chemical modification of sodium caseinate affected both the activity and the diffusion coefficients of the volatiles. These variations were interpreted in terms of a relation between the change in structure and the different physicochemical properties of the proteins. The glucosylated and galactosylated proteins exhibited the highest viscosity and induced a decrease in the diffusion coefficients, contrary to lactosylated and maltosylated proteins. The cause of increased viscosity is the variation of the quantity of bound water between the two types of substituted proteins.

Keywords: *Aroma; glycosylated proteins; interactions; diffusion*

INTRODUCTION

Developments in food technology have created a need for proteins with functional properties suitable for new utilization conditions. Some studies have been carried out on binding carbohydrates to proteins and how such new macromolecules can improve their solubility or heat stability (Canton and Mulvihill, 1983; Kitabatake et al., 1985). The study of the effect of chemical modifications enables an understanding and investigation of the relationship between structure and functional properties.

These new ingredients may also affect the mobility and volatility of low molecular weight molecules, such as aroma compounds, in food products. The knowledge of the aroma diffusivity is a determinant datum in the investigation of functional properties of the food matrix and processings, e.g., drying and thermal operations or food formulation (Saravacos and Moyer, 1968; Voilley, 1995); hence, it is required to better control the sensory quality of foods.

Diaz et al. (1993) studied the mass transport of NaCl and 2-propanol in various matrices containing either carbohydrates, proteins, or fats, with gel as carrier substance. They reported the importance of the hydration of the polymer on the diffusion of the solutes in the matrices. Farès (1987) demonstrated that retention of aroma compounds by casein during drying was higher than that by poly(ethylene glycol), maltose, and maltodextrins. Those published studies show the effects of water content and the nature of the medium on the kinetic behavior of solutes in food systems. Two basic mechanisms have been proposed to explain this retention effect of volatiles, i.e., formation of volatile-containing microregions (Flink and Karel, 1970) and selective diffusion (Thijssen and Rulkens, 1968). When the latter process occurs, the diffusion coefficient of water and aroma molecules was reduced as water content decreased due to drying.

This work concerned the effect of glycosylation of bovine sodium caseinate on diffusion behavior of aroma compounds in aqueous systems. Many studies on aroma diffusion were realized from carbohydrates such as glucose, maltose, or maltodextrins (Menting, 1969; Chandrasekaran and King, 1972; Bettenfeld, 1985). Few works have dealt with sodium caseinate to investigate the behavior of aroma compounds in the presence of food constituents. In addition, this protein was used because of its well-characterized functional properties and its addition as an ingredient in dairy and nondairy products (Kinsella, 1984).

The study determined thermodynamic and kinetic properties of volatiles in the presence of native and modified sodium caseinate in order to reveal and quantify the interactions between aroma compounds and proteins and molecular diffusion in the food matrix. These data are required to predict the efficiency of aroma retention during food industry processes and flavor release.

MATERIALS AND METHODS

Materials. The aroma compounds acetone, diacetyl, benzaldehyde, ethyl acetate, 2-propanol, and *n*-hexanol were purchased from Merck (Darmstadt, Germany). These molecules were chosen as models and for their different physicochemical properties (Table 1). Their purities were higher than 98%. Casein was from Prospérité Fermière (Arras, France). Agar-agar (Merck, Darmstadt, Germany) was used as gelling agent.

Preparation of Sodium Caseinate. After solubilization in distilled water at pH 7 with NaOH (1 and 0.1 M), the casein solution was filtrated, precipitated at isoelectric pH 4.6 with HCl (1 and 0.1 M), and rinsed. Sodium caseinate was solubilized in distilled water, readjusted at pH 7 with NaOH (1 and 0.1 M), and freeze-dried (SMJ USIFROID). The protein was stored at 5 °C in a closed container until use. Its mean molecular mass was about 23 000 g/mol.

Chemical Modification of Sodium Caseinate. The glycolysated sodium caseinate was prepared according to methods of Lee et al. (1979). The solutions were dialyzed

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S0021-8561(96)00935-1 CCC: $14.00

Table 1. Physicochemical Properties of Aroma Compounds

aroma compound	p_i^s (mmHg) at 25 °C[a]	aqueous solubility (g/L)	hydrophobicity log P[b]
acetone	231.2	miscible	−0.3
diacetyl	57.6	250 at 15 °C	−2.0
benzaldehyde	0.75	7.1 at 25 °C	1.5
ethyl acetate	94.6	86 at 20 °C	0.6
2-propanol	42.5	miscible	0.1
n-hexanol	1.0	5.9 at 20 °C	1.9

[a] p_i^s values calculated by the Antoine equation (Reid et al., 1987). [b] Logarithm of the partition coefficient between water and *n*-octanol (log P) calculated by the Rekker method (1977).

Table 2. Physicochemical Characteristics of Sodium Caseinate

bound carbohydrate	modification degree (%)	water content (g/100 g of protein)[a]	NaCl (g/100 g of protein)[b]
	0	6.1	3.5
galactose	47	9.1	3.7
	71	3.5	5.5
glucose	45	7.8	3.5
maltose	54	6.3	8.9
lactose	43	6.7	7.1

[a] Determined after 75 h at 64 °C. [b] Determined by electric conductivity.

during 48 h, once against 1.0 M NaCl and three times against distilled water, and freeze-dried. The degree of modification, i.e., the percentage of the free ϵ-lysyl amino groups substituted by the carbohydrates, was determined by the 2,4,6-trinitrobenzenesulfonic acid (TNBS) method as described by Habeeb (1966) and Kakade and Liener (1969). The physicochemical characteristics of native and modified sodium caseinate are given in Table 2. The pH of aqueous solutions of sodium caseinate, native or glycosylated, was 7.

Preparation of the Gels. The preparation of the gels was as described by Voilley and Bettenfeld (1985). Two solutions were prepared, one by dispersing 0.8 g of agar in 20 mL of water and the other by adding 2 g of protein to 20 mL of water. After mixing at 120 °C during 2 h, both were added together at 70 °C for 10 min. The resulting mixture was poured into a tube to fill the lower half. Amounts of volatiles (1%) were added to 20 mL of the remaining solution. After gelation of the lower half of the tube, the mixture containing the aroma compound was poured into the upper half. The tube was closed and stored at 25 °C for 110 h.

Choice of the Concentration of Sodium Caseinate. Tests were realized with sodium caseinate concentrations of 25, 50, 100, and 150 g/L and showed the absence of gelation for sodium caseinate concentrations higher than 50 g/L. Addition of salts such as $CaCl_2$ and $BaCl_2$ with a sodium caseinate of 75 g/L did not improve the rigidity of the gel. The chosen protein concentration was 50 g/L.

Methods of the Concentration Profiles. The gel was removed from the tube after 110 h and cut into slices of 2-mm thickness with a system of regularly spaced blades. Each slice was immersed in water and allowed to stand for 2 h at room temperature. The quantity of aroma compounds in each slice was determined by gas chromatography. The chromatographic analyses of the aqueous extract were carried out on a Hewlett Packard 5710 A GC (Avondale, PA) equipped with a flame ionization detector and a stainless steel column (3 m × 3.15 mm i.d.) packed with Chromosorb W-AW 100−200 mesh Carbowax 20 M - 10% (Chrompack Co., Middleburg, The Netherlands). The column was held at 80 °C and then programmed to 150 °C at 4 °C/min. The detector and injector were operated at 250 °C. The gas flow rates were as follows: N_2, 27 mL/min; H_2, 105 mL/min; air, 342 mL/min. The diffusion coefficient D of the aroma compounds was calculated by plotting the concentration−distance curve for a known time (Voilley and Bettenfeld, 1985).

Measurement of Volatility. Exponential dilution was used to determine the vapor−liquid equilibrium of the aroma compounds. This method consists of exhausting the liquid phase of volatile compounds in equilibrium with the vapor phase (Leroi et al., 1977). An inert gas (helium) passed through the liquid phase (130 g of solution containing a molar fraction of less than 5×10^{-4} volatile compound) and carried the volatile compound into the headspace. The system was thermostated at 25 °C. A sample of the vapor phase was automatically injected into a gas chromatograph at regular intervals. The variation of the chromatographic peak of the solute is an exponential function of time, provided the detector response is linear (Sorrentino et al., 1986):

$$\log S = \log S_0 - \frac{p_i^s d}{RTN} \times \gamma_i^\infty t \qquad (1)$$

where S and S_0 are the volatile peak areas; p_i^s, the vapor pressure of pure compound i (Pa); d, carrier gas flow rate (m^3/min); R, gas constant ($R = 8.314$ J/K/mol); T, temperature (K); N, number of moles of liquid phase; γ^∞_i, activity coefficient of compound i; t, time (min).

The activity coefficient was calculated from the values of the slope of the straight line obtained by plotting log S against time and represents the tendency for intermolecular interactions to develop between the component i and the major constituents of the liquid. The particular device used allows the investigation of the vapor−liquid equilibrium of viscous solutions ($\leq$1000 mPa·s^{-1}) and foaming systems such as aqueous solutions of proteins (Sorrentino et al., 1986). The activity coefficient of the aroma compounds in water was chosen as a reference. The percentage of retention R of the volatiles on the protein was then allowed to be determined (Landy et al., 1995):

$$R = \left(1 - \frac{\gamma^\infty_P}{\gamma^\infty_W}\right) \times 100 \qquad (2)$$

where γ^∞_P and γ^∞_W are the activity coefficients of the solute in protein solution and water. A significant variation of γ^∞_P compared with the reference γ^∞_W is due to aroma compound−medium interactions.

A gas chromatograph (Packard model 427, Downers Grove, IL) equipped with a flame ionization detector was used. The gaseous samples were injected onto a 3 mm × 0.7 m Porapack Q column (Alltech, Deerfield, IL). Gas flow rates were as follows: He, 65 mL/min; H_2, 56 mL/min; air, 280 mL/min. The column temperature varied as the nature of the aroma compound varied. The injector and detector temperatures were 200 °C.

Measurement of Sorption. Sorption of the aroma compounds to sodium caseinate was monitored during a reaction time of 600 h using static gravimetry in a dessicator containing about 300 g of silica gel to maintain a low and constant water activity. This measurement was realized twice; the sorption kinetic was controlled regularly at short intervals in order to confirm the equilibrium. The quantity of the sorbed aroma compounds was determined by gas chromatography. The results shown in Figure 1 are the mean of the two replicates.

RESULTS AND DISCUSSION

Diffusion of Aroma Compounds in Water and in Sodium Caseinate Solutions. Table 3 shows the activity coefficients and the diffusion coefficients of the aroma compounds in water and in aqueous solutions of sodium caseinate at 50 g/L. The values of activity coefficients in water were highest for benzaldehyde and *n*-hexanol. These compounds were endowed with the highest molecular masses and hydrophobicities (log P of 1.5 and 1.9). The other group of compounds consisted of rather hydrophilic volatiles, i.e., acetone, diacetyl, ethyl acetate, and 2-propanol, with log P values from −2.0 to 0.6.

Table 3. Activity and Diffusion Coefficients of the Aroma Compounds in Water and Sodium Caseinate Solutions at 25 °C

	γ^{∞}			D ($m^2/s \times 10^{10}$)	
aroma compound	water	sodium caseinate (50 g/L)	retention (%)	water	sodium caseinate (50 g/L)
acetone	7	7	0	12.7	4.8
diacetyl	14.0	72*		8.5	5.1
benzaldehyde	1457	903*	38	9.6[a]	1.3
ethyl acetate	64	65	0	11.7	3.3
2-propanol	7	14*		10.2	4.9
n-hexanol	610	674	0	5.6	2.5

*Significantly different from γ^{∞}_W ($P < 0.05$). [a] Estimated value with the Wilke and Chang equation (Reid et al., 1987).

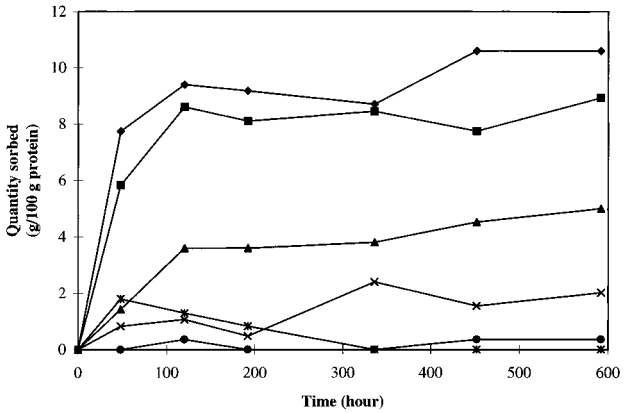

Figure 1. Sorbed amount of aroma compounds on sodium caseinate as a function of time at 25 °C: acetone (◆), ethyl acetate (■), 2-propanol (▲), benzaldehyde (×), diacetyl (*), and *n*-hexanol (●).

All the diffusion coefficients decreased in the presence of sodium caseinate; benzaldehyde showed the lowest value of the diffusion coefficients, which can be explained by a retention of 38% of the molecule by the protein. For diacetyl and 2-propanol, a phenomenon of release from the substrate in aqueous solutions was observed, and their diffusion coefficients were the highest of the volatiles. The other molecules, acetone, ethyl acetate, and *n*-hexanol, did not interact with sodium caseinate in aqueous medium and presented intermediate values of diffusion coefficients. The diffusion results of the studied volatiles in sodium caseinate were explained by their retention in aqueous protein solutions determined from the vapor−liquid measurements. The hypothesis that a correlation existed between the aroma compound−protein interaction and the diffusion process could be proposed.

The sorbed quantity of aroma compounds on dry sodium caseinate as a function of time is shown Figure 1. The equilibrium of sorption was reached after 460 h. It is worthwhile to note a decrease in the sorbed quantity of diacetyl after 48 h. This result might be due to surface reactions with the protein, resulting in a loss of sorbed diacetyl. Farès et al. (1997) showed the formation of strong bonds between diacetyl and sodium caseinate. At equilibrium, the best retained compounds were in the decreasing order: acetone, ethyl acetate, 2-propanol, benzaldehyde, diacetyl, *n*-hexanol. This classification did not follow that of the diffusion coefficient. The absence of relationship could be due to the influence of the protein hydration on the nature of the interactions between the substrate and the aroma molecules. It is then difficult to correlate the measurements of sorption and diffusion. Farès et al. (1996) obtained different results of aroma retention from sorption and equilibrium dialysis experiments; acetone and ethyl acetate that sorbed best to caseins manifested no affinity to this protein in aqueous solutions, whereas the opposite effect was observed for diacetyl and benzaldehyde. Thus, water molecules remaining associated with sodium caseinate (6 g/100 g of protein) after freeze-drying might interfere differently with intermolecular interactions, such as protein−ligand binding, compared with bulk water of which the properties are different (Phillips et al., 1994). El-Rifai (1980) suggested that the high retention of diacetyl and benzaldehyde after freeze-drying was due to their stabilization by water molecules bound to the ketone and aldehyde groups, respectively. Both diacetyl and benzaldehyde also possessed the highest retention rate in the study carried out by Farès et al. (1996) with equilibrium dialysis. Water at the surface of the protein, bulk water, and the physicochemical properties of the aroma compounds seem to be determinant factors involved in the flavor−protein interactions and diffusion.

Table 4. Diffusion Coefficients of the Aroma Compounds in Aqueous Solutions of Sodium Caseinate at 50 g/L (25 °C)

	D ($m^2/s \times 10^{10}$)				
		glycosylated sodium caseinate			
aroma compound	native sodium caseinate	galactose	glucose	maltose	lactose
acetone	4.8	2.1	4.3	5.6	3.2
diacetyl	5.1	5.7	5.5	6.6	7.1
benzaldehyde	1.3		0.5	1.5	3.0
ethyl acetate	3.3	2.0	3.0	6.2	3.4
2-propanol	4.9	3.5	2.6	2.7	2.7
n-hexanol	2.5	3.3	3.0	4.6	3.1

Changes in Aroma Diffusion in the Presence of Modified Sodium Caseinate. The influence of the covalent binding of glycosyl residues to sodium caseinate on the diffusion coefficient depended on the nature of the bound carbohydrate: with maltosylated and lactosylated sodium caseinates, the diffusion coefficient increased, whereas sodium caseinate substituted with monosaccharides (i.e., glucose and galactose) induced a decrease in the diffusivity of the volatiles (Table 4). This effect was due to the difference of viscosities: the viscosity of the solution of maltosylated sodium caseinate was lower than that of the glucosylated and galactosylated sodium caseinates (Courthaudon et al., 1989); these authors reported viscosities of galactosylated, glucosylated, and maltosyalted caseinate solutions at 50 g/L of 3.1, 3.2, and 2.8 $mPa \cdot s^{-1}$, respectively, for a similar degree of modification. This discrepancy is explained by a difference of steric hindrance inducing changes in the quantity of bound water to the proteins. These variations of rheological characteristics of the different proteins indicated the modifications of structure due to the fixation of carbohydrates (Kinsella, 1976). Considering all these data, a link can be established between the structure and the functional properties. Galactosylation of caseinate led to the largest decrease in the diffusion coefficient of acetone and ethyl acetate. The diffusion coefficients were lowest for 2-propanol and benzaldehyde in the presence of glucosylated sodium caseinate, and those of diacetyl and *n*-hexanol were found to be higher than those in native sodium caseinate. For diacetyl, Farès et al. (1996) showed the presence of covalent bonds with the ϵ-amino group of lysyl residues of sodium caseinate in aqueous solutions from measurements by the equilibrium dialysis method. The increase in the diffusion coefficient of

Table 5. Activity Coefficients of Acetone and Benzaldehyde in Aqueous Solutions of Glycosylated Sodium Caseinate at 25 °C

	γ^{∞}_P	
bound carbohydrate	acetone	benzaldehyde
galactose	5.6*	9223*
glucose	7.0	12265*
maltose	7.4	13355*
lactose	6.7	7871*

*Significant difference ($P < 0.05$) between native and modified sodium caseinate.

diacetyl should be due to the presence of substituted lysyl residues preventing diacetyl from interacting irreversibly with the protein.

Table 5 gives the activity coefficients of acetone and benzaldehyde in aqueous solutions of glycosylated sodium caseinate. The activity coefficient of acetone in the presence of modified proteins was significantly different from that in native sodium caseinate when galactose was the bound carbohydrate (retention of 21% in relation to water). This effect could also explain the low diffusion coefficient of acetone ($D = 2.1 \times 10^{-10}$ $m^2 \cdot s^{-1}$) in the presence of galactosylated sodium caseinate because of interactions between the protein and the solute. The activity coefficient of benzaldehyde in modified sodium caseinate solutions increased in relation to that in native protein solutions and in water. Interactions between benzaldehyde and glycosylated sodium caseinate did not occur, and benzaldehyde was released from the protein solutions. Contrary to acetone, the diffusion of benzaldehyde should be affected by viscosities of the protein solutions because of the absence of interactions between the latter and the solute. Its diffusion coefficient was 0.5×10^{-10} $m^2 \cdot s^{-1}$ in glucosylated sodium caseinate solution in relation to a value of 1.3×10^{-10} $m^2 \cdot s^{-1}$ in sodium caseinate solution, and the viscosities of these solutions were respectively 3.2 and 4.5 $mPa \cdot s^{-1}$ (Courthaudon et al., 1989).

Farès (1987) observed that, after freeze-drying, glycosylated caseins presented a lower capacity of retention of the same aroma compounds as native casein, except for galactosylated and lactosylated caseins. Viscosity did not seem to be the only factor responsible for the behavior of the caseins with volatiles during drying; however, the high viscosity of galactosylated protein was consistent with the large retention by the modified casein. After drying, the retention was highest for benzaldehyde and *n*-hexanol whether sodium caseinate was glycosylated or not; their high activity coefficient and low diffusion coefficient could explain this result. However, *n*-hexanol exhibited the lowest quantity that was sorbed to sodium caseinate and was not bound to the protein in aqueous solution (Farès et al., 1996). Drying process is thus an operation which gives rise to different kinds of physicochemical phenomena between the substrate and *n*-hexanol, inducing a strong retention of the latter.

CONCLUSION

The thermodynamic and kinetic properties of aroma compounds in water and aqueous solutions of proteins were determined by measurements of their activity and diffusion coefficients. The influence of the nature of the aroma molecules on both coefficients was reported. In the presence of 50 g/L protein, the effect of interactions between aroma compounds and proteins on aroma diffusion was pointed out. The diffusion data were not interpreted by the sorption results, suggesting the role of water on physicochemical properties of aroma compounds with the matrix.

The binding of carbohydrates to sodium caseinate modified its structure and functionality. The diffusion data reflected these modifications of viscosities and interactions between aroma compounds and proteins. This work aimed at testing new flavor carriers in order to optimize the stabilization of volatiles during encapsulation techniques such as spray-drying. Future research should be directed toward aroma diffusivity in heterogeneous systems, e.g., solutions exhibiting an altered structure from a certain water content or concentration of macromolecules.

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Received for review December 11, 1996. Revised manuscript received March 28, 1997. Accepted March 31, 1997.[⊗]

JF960935S

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.