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Use of Nuclear Magnetic Resonance to Model Thermophysical Properties of Frozen and Unfrozen Model Food Gels

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ABSTRACT

This study deals with the measurement and the modelling of the heat capacity of model food gels in frozen or unfrozen states. To improve the modelling, the amount of each water state (ice, freezable water and bound or unfreezable water) was measured by low-resolution pulsed nuclear magnetic resonance (NMR) as a function of temperature. The amounts of water bound to each solid were found as 0·66 g g^{-1} *DM (dry matter) for agar; 0·05 g g*$^{-1}$ *DM for sucrose; 0·26 g g*$^{-1}$ *DM for starch; 0·44 g g*$^{-1}$ *DM for gelatin; 0·31 g g*$^{-1}$ *for ovalbumin. Heat capacity values calculated from these results were closer to experimental ones than those obtained from an additive model of the heat capacity when the water fractions were estimated by the Raoult's law. Besides, the NMR data were used to check some thermal conductivity models of food gels (the series model, parallel model or Maxwell's one). Generally, the prediction of thermophysical properties was better when the different states of water were determined experimentally by NMR.*

NOTATION

a_w	Water activity
C_p	Heat capacity (J kg^{-1} °C^{-1})
L	Latent heat of fusion of ice (J kg^{-1})
m	Mass (kg)
R	Ideal gas constant (J mol^{-1} K^{-1})
S	Calorimeter's sensitivity (A^{-1})
t	Time (s)
T	Temperature (K or °C)
U	Tension measured with sample (V)
U'	Tension measured without sample (V)
x	Mass fraction
y	Molar fraction

Subscripts

app	Apparent
b	Bound water
uw	Unfrozen water
i	Ice
s	Solid
suc	Sucrose
w	Liquid water

INTRODUCTION

Due to the heterogeneity and the variety of different foodstuffs, it is difficult to find in the literature comprehensive data on thermophysical properties of frozen food materials such as heat capacity, thermal conductivity or even density (Staph & Woolrich, 1951; Woolrich, 1986; Lind, 1991).

Moreover, measurements of the amounts of the different water states as a function of temperature were not made precisely, these values are often calculated and estimated by theoretical models of varying accuracy. The only values that one can obtain from the literature are the amounts of water bound to solids (Dickerson, 1968; Duckworth, 1971; Kumagai *et al.*, 1985; Pham, 1987).

It was observed by some authors that the application of models based on the thermodynamics of dilute solutions (Raoult's law) gave reliable estimations (Heldman, 1974; Schwartzberg, 1976; Chen, 1985*a*, *b*; Mannapperuma & Singh, 1989; Renaud *et al.*, 1992).

Model food gels, studied by Renaud (Renaud, 1990; Renaud *et al.*, 1992), were used to model foodstuffs because their composition and their structure were well known for the measurement of the thermal conductivity and the thermal diffusivity.

The aim of this study was to measure the amounts of each water state, at negative temperatures down to −40°C, of these gels as a function of temperature by low-resolution nuclear magnetic resonance (NMR). These amounts were used to calculate heat capacities and the values were compared first to experimental data and secondly to data obtained by Raoult's relationship.

Using the Heldman's hypothesis, it was assumed in this study that the bound water was the remaining liquid water at −40°C (Heldman, 1974; Pham, 1987).

EXPERIMENTAL METHODS

Sample preparation

The gels were prepared by the method indicated by Renaud (1990) in order to control and maintain good reproducibility in their structure and their texture.

All gel compositions are indicated in Table 1. For sucrose or starch gels, it was necessary to add agar (as a gelling agent) to the gel mixture, the mass fraction of agar being 4%. So, the gel structure was reasonably reproducible, homogeneous and rigid. The samples were stored in a desiccator where the desiccant agent was replaced by water in order to prevent any dehydration before measurements.

NMR experiments

Hot liquid gels were placed in a 7·5 mm diameter NMR glass tube and left 16 h in a moisture surrounding (desiccator with water).

The NMR apparatus was a Bruker Minispec PC 20 equipped with a temperature regulation system. To measure the amount of liquid water in a sample at any temperature between −40 and 20°C, a 90° pulse was applied to flip the magnetisation over from the z-axis to the y-axis where it can be detected. Then, the free induction decay (FID) signal was measured after 70 μs (three times) to minimise the influence of experimental errors. This signal was proportional to the amount of 'liquid' protons (Fung & McGaughy, 1974).

For temperatures above 0°C, the FID value used was a mean of FID values measured at some fixed positive temperature. This mean value was conventionally assumed to be equal to one and any signal at subzero temperature was divided by this value. So, this ratio gave directly the amount of liquid water at any temperature — the FID relative (FIDR). This method was also chosen by other workers to measure the amount of liquid water in muscles (Fung & McGaughy, 1974). The waiting time between each measurement was about 5–10 s depending on the temperature and on the spin-lattice relaxation time of the system (Cornillon, 1993).

TABLE 1
Mass Composition of Gels

Gel	*Dry matter content (%)*
Water–agar	4
Water–sucrose–agar	10; 20; 30; 40; 50
Water–starch–agar	10; 20; 30
Water–gelatin	10; 20; 30; 40
Water–ovalbumin	10; 13·5; 20; 30

Differential calorimetry measurements

The differential calorimeter with a high sample mass (about 10 g) was constructed in our laboratory (Laurent, 1992) and was based on the differential calorimetry principle. The apparatus is shown in Fig. 1.

Samples were placed in a mould made from a thin piece of aluminium foil. Then, the gelation took place over 16 h in a moisture surrounding (desiccator with water). Finally, these samples were placed in the calorimeter.

A blank and a sensitivity calibration were made before measurements. The heat capacity was calculated from the following relation (Cornillon, 1993):

$$m_{\text{sample}} C_{\text{p sample}} = -S \left(\frac{U}{\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)} - \frac{U'}{\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)'} \right)$$

where S represents the calorimeter's sensitivity, U and U', respectively, the voltages measured with or without any sample, $(\mathrm{d}T/\mathrm{d}t)$ and $(\mathrm{d}T/\mathrm{d}t)'$ the rates of temperature variation during measurements with and without sample.

EXPERIMENTAL RESULTS

NMR results

All results obtained by NMR are presented in Figs 2–13.

These data showed some differences between the sucrose gels and the other ones. For sucrose gels, even at −40°C, the liquid water was still freezing and the

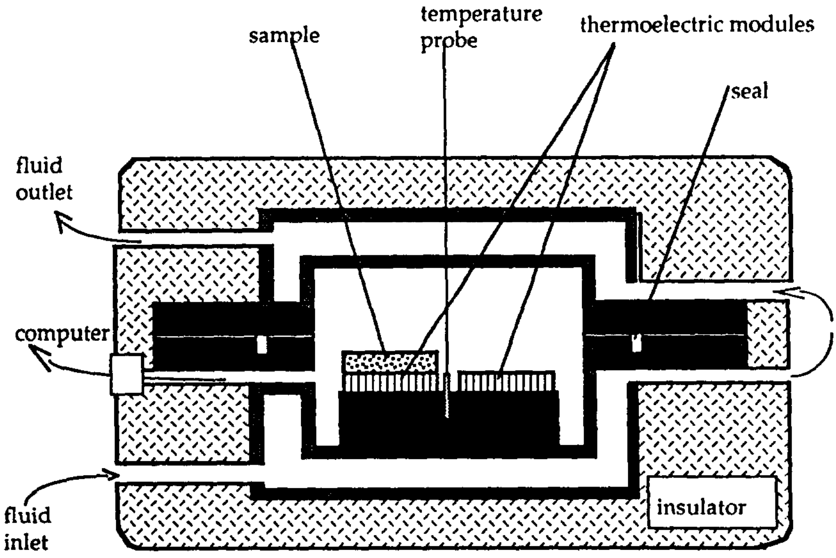

Fig. 1. Calorimeter diagram.

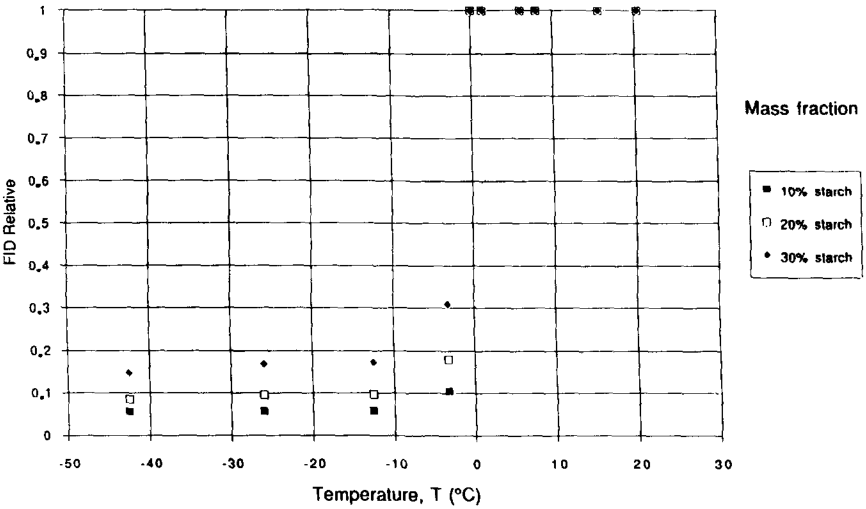

Fig. 2. Variation of the FID with temperature for sucrose gels.

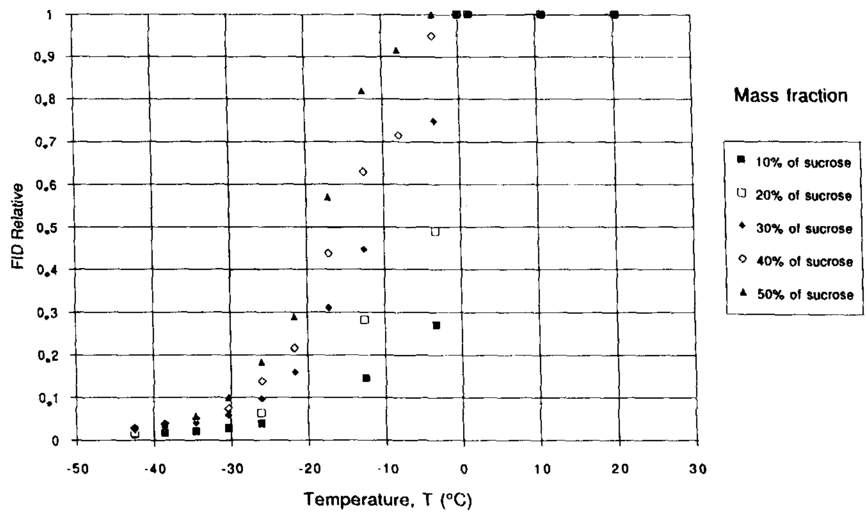

Fig. 3. Variation of the FID with temperature for starch gels.

amount of that water was relatively constant with temperature whatever the mass fraction of sucrose was.

On the contrary, for the other gels, the amount of bound water increased with the mass fraction of dry matter in the gel. Besides, it was observed that the freezing of 90% of the total liquid water content was realised between 0 and − 10°C.

For sucrose gels, the water bound to the dry matter was approximately equal to 0·05 g g^{-1} DM (Figs 2, 6 and 7). This value is less than those obtained by other workers (Leung *et al.*, 1976; Leung & Steinberg, 1979). By NMR, they

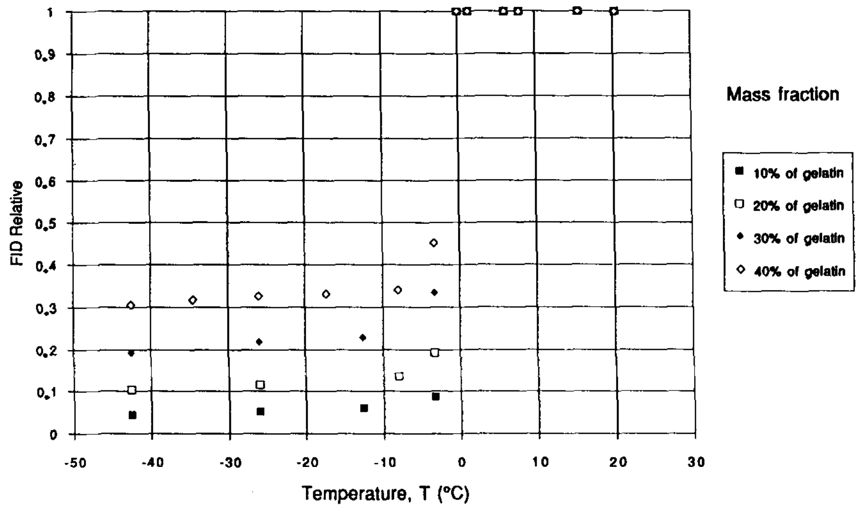

Fig. 4. Variation of the FID with temperature for gelatin gels.

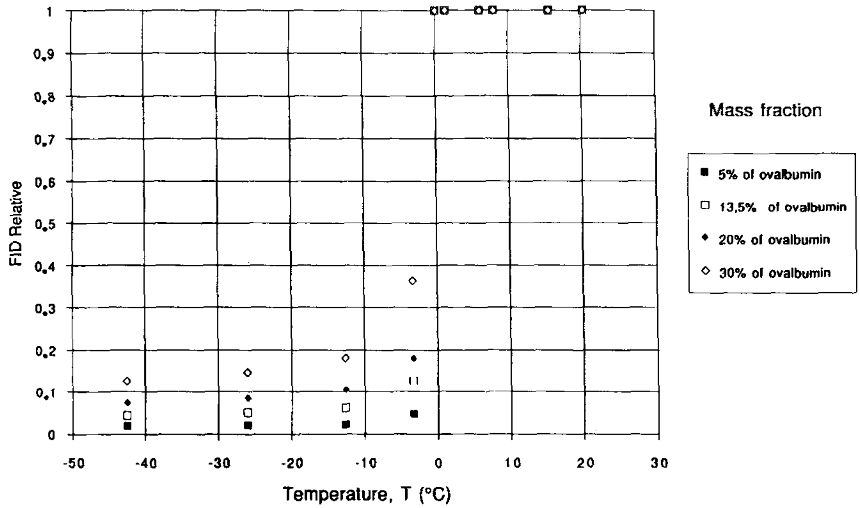

Fig. 5. Variation of the FID with temperature for ovalbumin gels.

found that the bound water fraction was about 0·3 g g^{-1} DM. These differences may be due to the presence of a glass transition near −35°C which influenced the NMR signal by freezing the structure of the concentrated solution present in the frozen gel. Figure 2 shows that below −35°C, the NMR signal was nearly constant whatever the concentration of dry matter was. Nevertheless, above −35°C, the signal was directly proportional to the dry matter content. Figures 6 and 7 show that the amount of ice at any temperature was dependent on the dry matter content. For example, at −20°C for the 10% sucrose gel, the amount of ice in the gel was 90%; for the 50% sucrose gel, this fraction was only 50%.

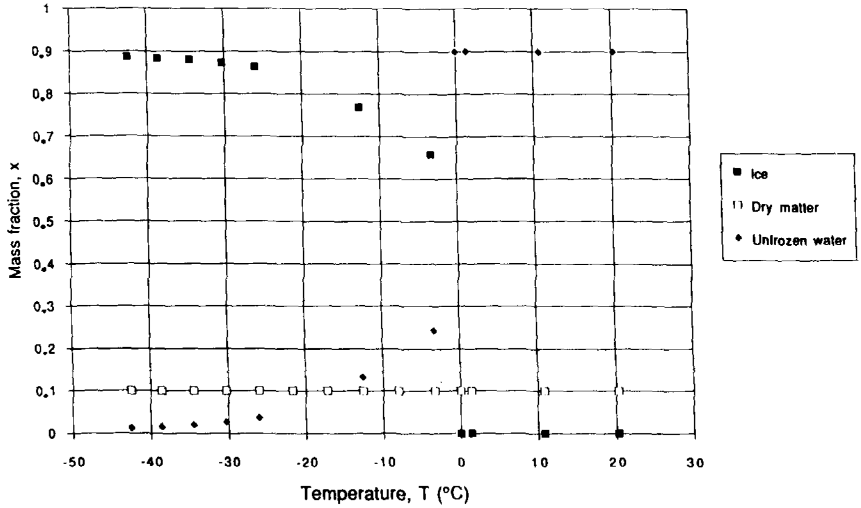

Fig. 6. Mass composition of the 10% sucrose gel.

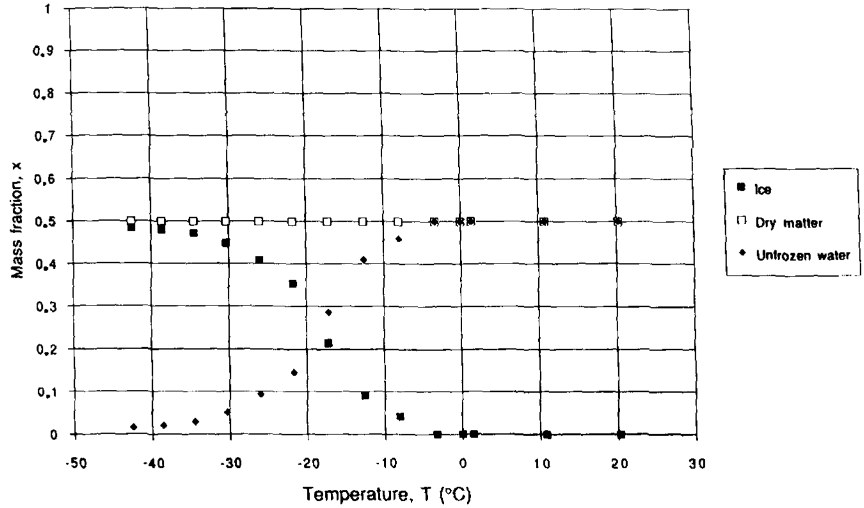

Fig. 7. Mass composition of the 50% sucrose gel.

For starch gels, a bound water content equal to 0·26 g g^{-1} of DM was observed (Figs 3, 8 and 9). This value is in good agreement with the literature (Leung *et al.*, 1976, 1979; Leung & Steinberg, 1979; DiNola and Brosio, 1983). Figure 3 shows that under − 15°C, all the freezable water was transformed into ice. The amount of unfrozen water below that temperature was almost constant and dependent on the amount of dry matter as indicated in Figs 8 and 9.

The amount of water bound to gelatin was around 0·44 g g^{-1} of DM (Figs 4, 10 and 11). The literature values present some dispersions between 0·35 and 0·7 g g^{-1} DM (Dehl, 1970; Leung & Steinberg, 1979; Maquet, 1983; Maquet *et*

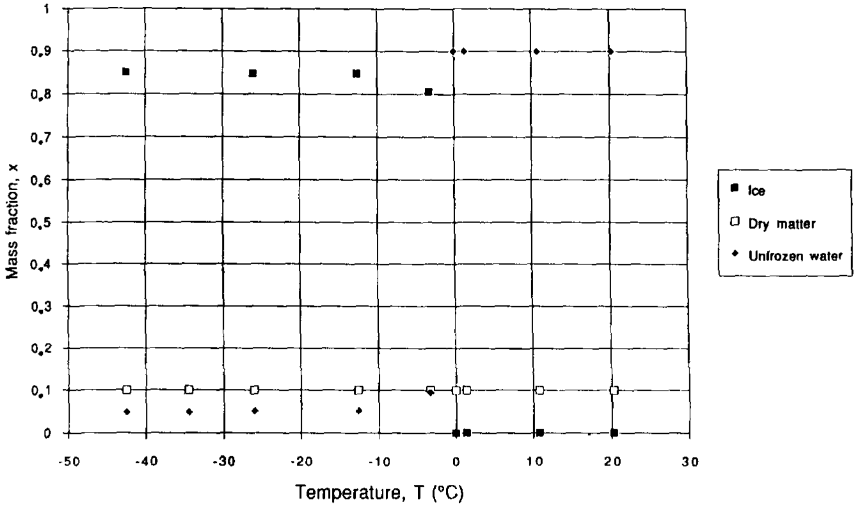

Fig. 8. Mass composition of the 10% starch gel.

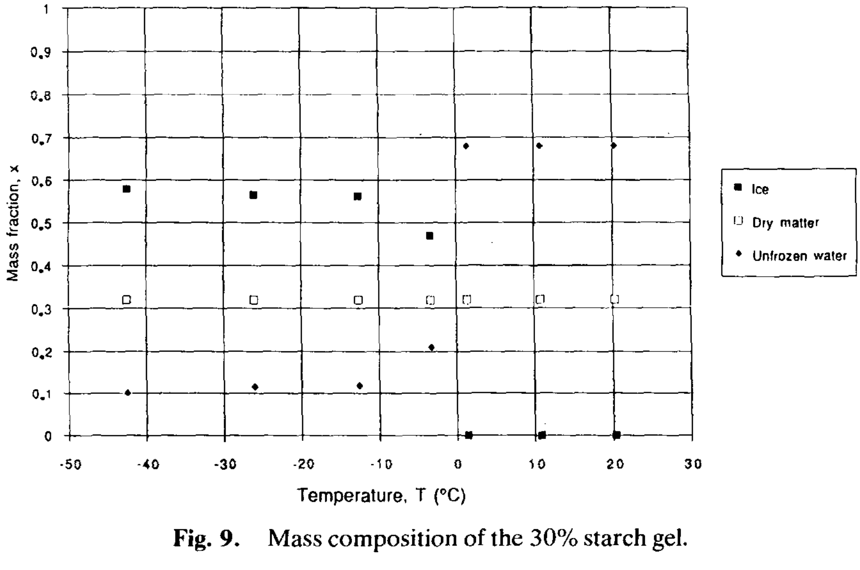

Fig. 9. Mass composition of the 30% starch gel.

al., 1986; Renaud, 1990). The amounts of liquid water for a given dry matter content was independent of the temperature. Approximately 95% of the total water content was frozen at − 15°C (Fig. 4).

For ovalbumin gels, a bound water fraction about 0·31 g g^{-1} of DM was obtained (Figs 5, 12 and 13). This value was also in agreement with the literature data obtained by NMR (Shanbhag *et al.*, 1970; Suzuki & Nagashima, 1982).

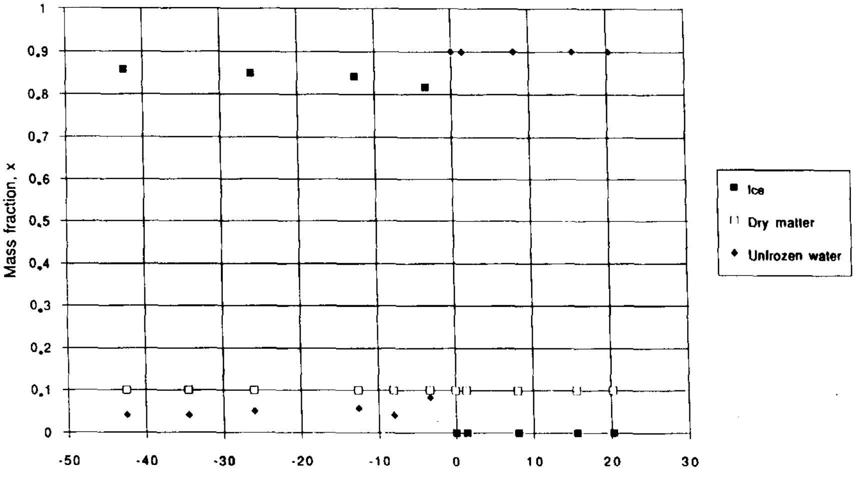

Fig. 10. Mass composition of the 10% gelatin gel.

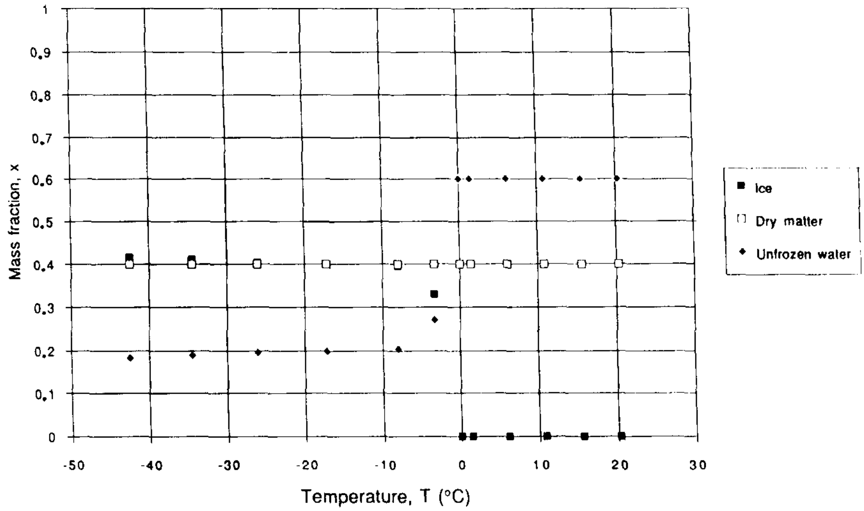

Fig. 11. Mass composition of the 40% gelatin gel.

As a conclusion, we observed that the NMR method used was able to give the bound water fraction and the amount of liquid water at any temperature.

Differential calorimetry results

All experimental heat capacity data are presented in Figs 14–17 (Cornillon, 1993).

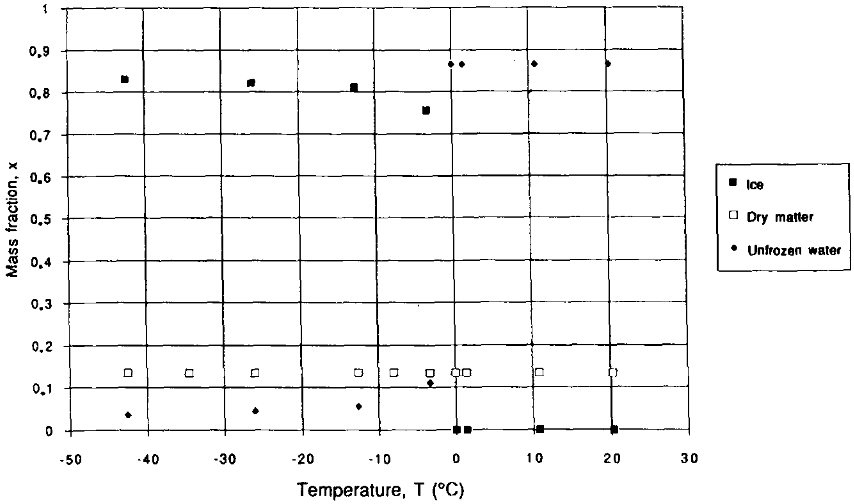

Fig. 12. Mass composition of the 13·5% ovalbumin gel.

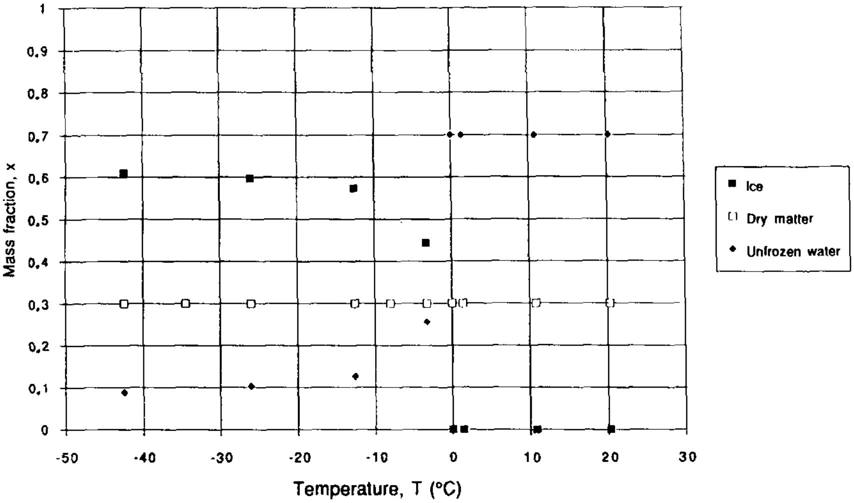

Fig. 13. Mass composition of the 30% ovalbumin gel.

When the temperature decreased from 20 to −40°C, the freezing of the mixture did not appear at the true initial freezing temperature of the mixture but at a lower temperature because of subfreezing. This phenomenon increased with the amount of dry matter present in the mixture.

For positive temperatures, the heat capacity increased with the amount of the total water content of the gel. At negative temperatures, the heat capacity

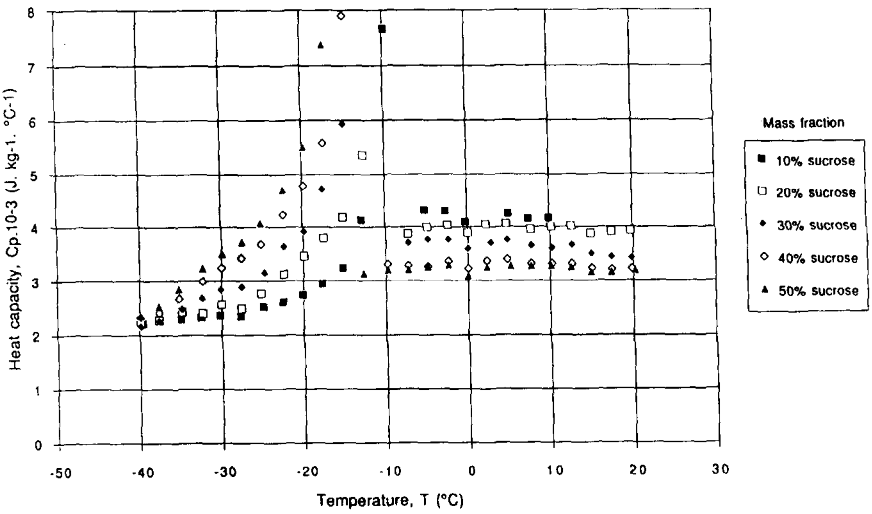

Fig. 14. Variation of the heat capacity with temperature for sucrose gels.

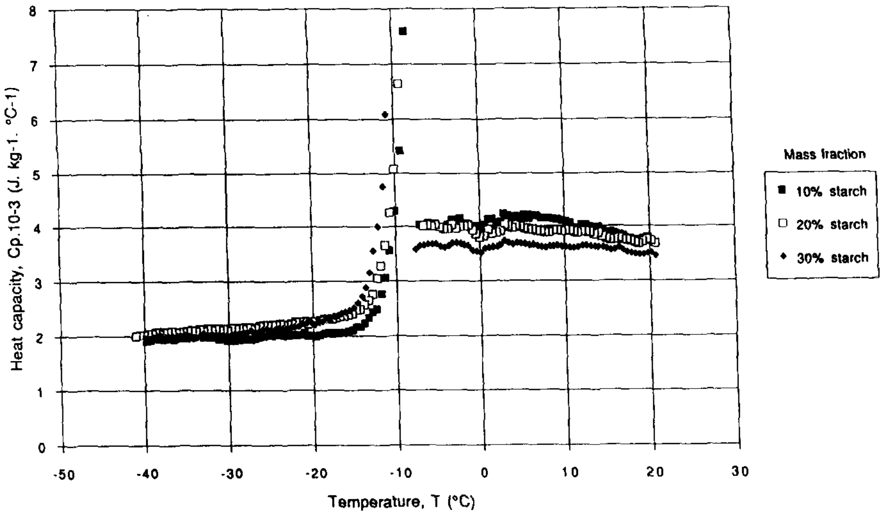

Fig. 15. Variation of the heat capacity with temperature for starch gels.

increased with the dry matter fraction. So, the more the dry matter fraction, the less the water or ice fraction; this inversion was probably due to a decrease of the heat capacity with the dry matter fraction because while water has a heat capacity of approximately 4200 J kg^{-1} $°C^{-1}$, the heat capacity of ice is nearly 2000 J kg^{-1} $°C^{-1}$ and the solid's one is around 2000 J kg^{-} $°C^{-1}$. Using the

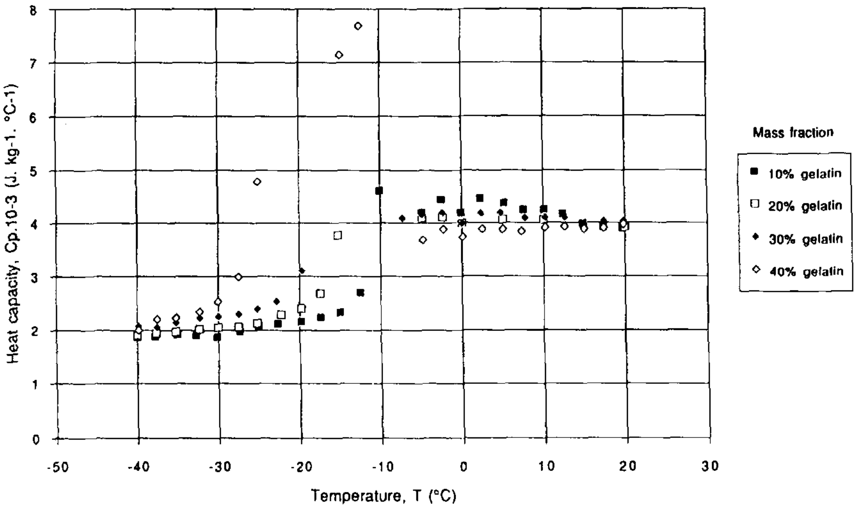

Fig. 16. Variation of the heat capacity with temperature for gelatin gels.

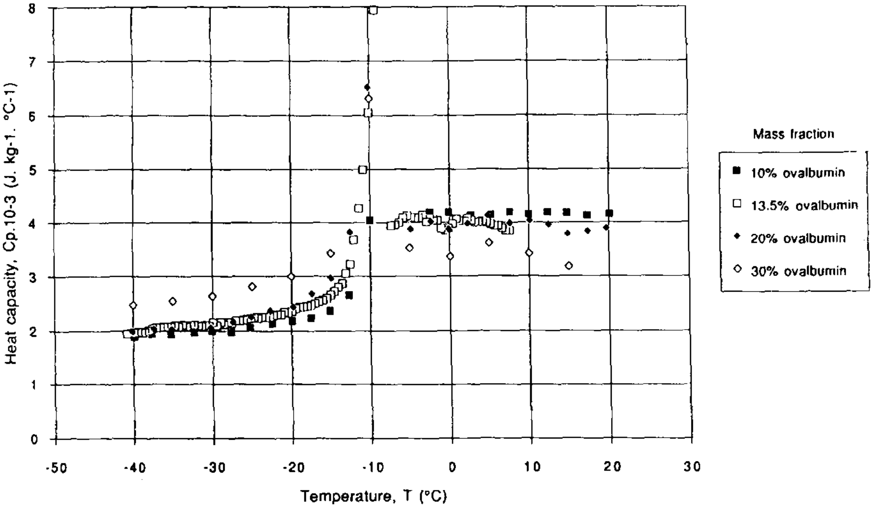

Fig. 17. Variation of the heat capacity with temperature for ovalbumin gels.

additive model and not considering the latent heat of fusion of ice, it was possible to conclude that the heat capacity increased with the water fraction for positive temperatures and increased with the dry matter fraction for negative temperatures.

TABLE 2
Comparison of the Different Kinds of Water as a Function of the Temperature for Ovalbumin Gels

T (°C)	*Water–ovalbumin 13·5%*			*Water–ovalbumin 20%*			*Water–ovalbumin 30%*		
	Ice fraction (NMR)	*Ice fraction (calculated)*	*Error (%)*	*Ice fraction (NMR)*	*Ice fraction (calculated)*	*Error (%)*	*Ice fraction (NMR)*	*Ice fraction (calculated)*	*Error (%)*
0	0	0	—	0	0	—	0	0	—
−3·3	0·755	0·714	5·7	0·656	0·59	11·2	0·444	0·398	11·6
−12·6	0·811	0·808	0·4	0·715	0·728	1·8	0·573	0·605	5·3
−26	0·821	0·824	0·4	0·732	0·752	2·7	0·597	0·642	7·0
−42·5	0·83	0·829	0·1	0·741	0·76	2·5	0·611	0·654	6·6

ANALYSIS

To model the heat capacity and the fraction of ice at any temperature, a thermodynamic model based on Raoult's law was used. This relationship was applicable for dilute solutions. This model considered the variation with temperature of the latent heat of fusion of ice (Mannapperuma & Singh, 1989).

By integration of the following relation:

$$\mathrm{d}(\ln a_{\mathrm{w}}) = \mathrm{d}(\ln y_{\mathrm{uw}}) = \frac{L\,\mathrm{d}T}{RT^2}$$

where the latent heat of fusion of ice is $L = A_0 + A_1 \times T + A_2 \times T^2 + A_3 \times T^3$, the amounts of any water states (ice, freezable water and unfreezable water) were calculated for temperatures between 20 and − 40°C and then, these values were compared with those for NMR. For instance, Tables 2, 3 and 4 show this data comparison for ovalbumin gels.

Experimental results were close to the calculated ones, except for sucrose gels. In fact, the structure and texture of these gels were not well defined below − 30°C and these characteristics were not taken into account by the theoretical model. Moreover, the solid concentration did not permit the application of Raoult's law because the solution was not diluted. To take into account all these factors, it is necessary to use other models such as the UNIFAC (Universal Functional Group Activity Coefficients) model (Fredenslund & Rasmussen, 1975; Larsen *et al.*, 1987; Archard *et al.*, 1992) to introduce some interaction parameters for real solutions.

It was observed that the deviations between the theoretical values and experimental ones were larger when the dry matter fraction increased. This could be easily explained as Raoult's law is not valid for concentrated solutions.

The apparent heat capacity of gels was calculated from the knowledge of different water fractions by the following relation:

$$C_{\mathrm{papp}} = x_{\mathrm{s}} C_{\mathrm{ps}} + x_{\mathrm{i}} C_{\mathrm{pi}} + x_{\mathrm{w}} C_{\mathrm{pw}} - L \frac{\mathrm{d}x_{\mathrm{i}}}{\mathrm{d}T}$$

Heat capacity values for solids, ice and water in a subfreezing state and the values of latent heat of fusion of ice were taken from Renaud (1990).

The calculation was made firstly with data obtained by NMR and secondly by the application of the model of Mannapperuma and Singh (1989). These results are gathered in Tables 3 and 5 for comparison with experimental values in the case of ovalbumin gels. Results for the other gels studied can be found elsewhere (Cornillon, 1993).

Errors obtained by comparing the heat capacity experimental values with the values calculated from NMR data were shorter than those obtained by comparing heat capacity values from Mannapperuma and Singh's model with experimental ones. It can be noted that deviations increased with the dry matter content probably due to the non-validity of Raoult's law.

As a conclusion, the knowledge of the amounts of different water states by NMR measurements improved the modelling of the gel's heat capacity.

TABLE 3
Comparison of the Heat Capacity as a Function of the Temperature for the 13·5% Ovalbumin Gel

T (°C)	*C_p (exp) ($J\ kg^{-1}\ °C^{-1}$)*	*NMR results*		*Calculated results*	
		C_p ($J\ kg^{-1}\ °C^{-1}$)	*Error (%)*	*C_p ($J\ kg^{-1}\ °C^{-1}$)*	*Error (%)*
20·0		3777		3777	
10·0	3754	3770	0·4	3770	0·4
0·0	3900	3765	3·5	3765	3·5
−3·3	4148	40520		15144	
−12·8	3226	2991	7·3	2778	13·9
−26·0	2211	2070	6·4	2025	7·0
−42·5	1900	1915	0·8	1867	1·7

TABLE 4
Comparison of the Heat Capacity as a Function of the Temperature for the 20·0% Ovalbumin Gel

T (°C)	*C_p (exp) ($J\ kg^{-1}\ °C^{-1}$)*	*NMR results*		*Calculated results*	
		C_p ($J\ kg^{-1}\ °C^{-1}$)	*Error (%)*	*C_p ($J\ kg^{-1}\ °C^{-1}$)*	*Error (%)*
20·0	3885	3584	7·7	3584	7·7
10·0	4035	3575	11·4	3575	11·4
0·0	3882	3567	8·1	3567	8·1
−3·3	4064	35676		21425	
−12·6	3829	3159	17·5	3129	18·3
−26·0	2271	2162	4·8	2090	8·0
−42·5	1885	1963	4·1	1842	2·3

TABLE 5
Comparison of the Heat Capacity as a Function of the Temperature for the 30% Ovalbumin Gel

T (°C)	*C_p (exp) ($J\ kg^{-1}\ °C^{-1}$)*	*NMR results*		*Calculated results*	
		C_p ($J\ kg^{-1}\ °C^{-1}$)	*Error (%)*	*C_p ($J\ kg^{-1}\ °C^{-1}$)*	*Error (%)*
20·0		3288		3288	
10·0	3422	3275	4·3	3275	4·3
0·0	3367	3263	3·1	3263	3·1
−3·3	4064	26546		31088	
−12·6	4810	4398	8·6	3669	23·7
−26·0	2780	2280	18·0	2142	22·9
−42·5	2450	2052	16·2	1803	26·4

THERMAL CONDUCTIVITY SIMULATION

The experimental water fractions were also used to model the thermal conductivity of gels. The comparison was made with experimental data obtained by Renaud (Renaud, 1990; Renaud *et al.*, 1992). Again, the NMR values of the fractions of freezable water, ice and bound water were used to calculate the thermal conductivity by the different models, namely, the series, parallel, series/parallel or Maxwell models. These values were compared to the experimental results in Figs 18–20 for ovalbumin gels.

Series and parallel models were not useful for modelling the thermal conductivity in the frozen state. Nevertheless, the series model approximates well to the true values of the thermal conductivity of gels for temperature above 0°C.

The series/parallel model was the more accurate in representing the thermal conductivity. Nevertheless, this model was based on an adjustable parameter which was not constant and not always easy to estimate due to the heterogeneity of gels during freezing.

The Maxwell model was better than the series or the parallel model. But, when the dry matter content increased, this model had larger errors, these errors reaching 60% for temperatures close to the initial freezing temperature. The heterogeneity of the gel and the subfreezing phenomenon did not allow any estimation of the thermophysical properties in this temperature range.

Using only experimental results, the errors for the series/parallel model were around 5% but could exceed 10% near − 1·0°C. For Maxwell's model, the mean errors were around 20%. Nevertheless, this model was chosen because it did not need any adjustable parameter. For starch and gelatin gels, the same conclusions

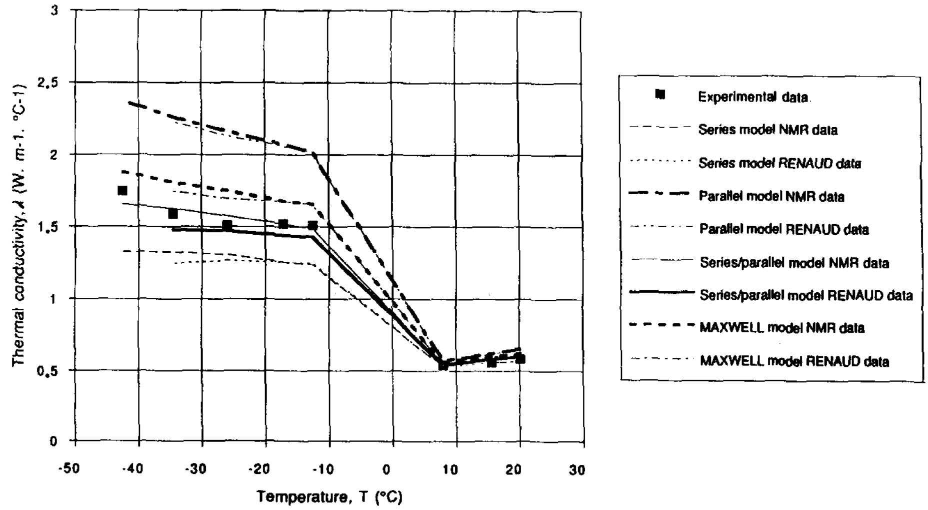

Fig. 18. Comparison of the thermal conductivity as a function of the temperature for the 13·5% ovalbumin gel.

were obtained. But, for the sucrose gels, the Maxwell model was the more accurate because the observed errors were lower than those obtained with the other models. The series/parallel model did not allow the modelling of the thermal conductivity of sucrose gels.

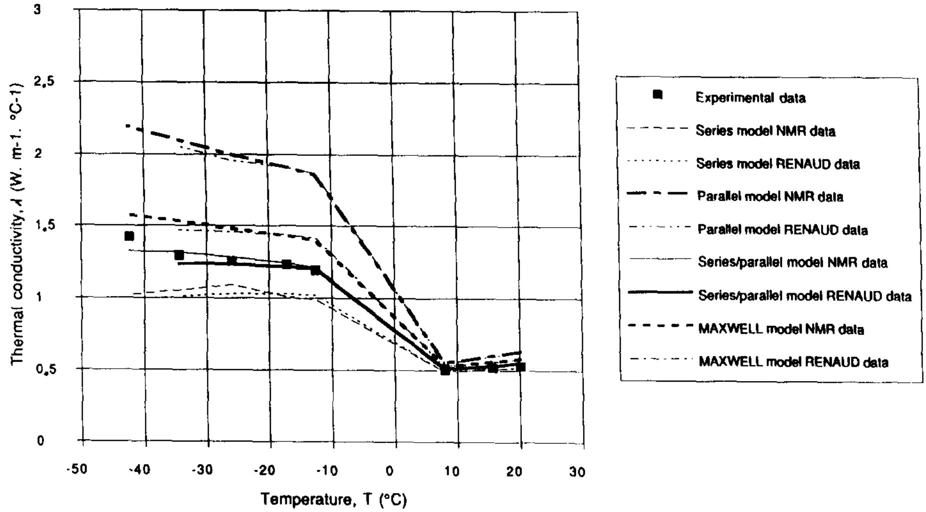

Fig. 19. Comparison of the thermal conductivity as a function of the temperature for the 20% ovalbumin gel.

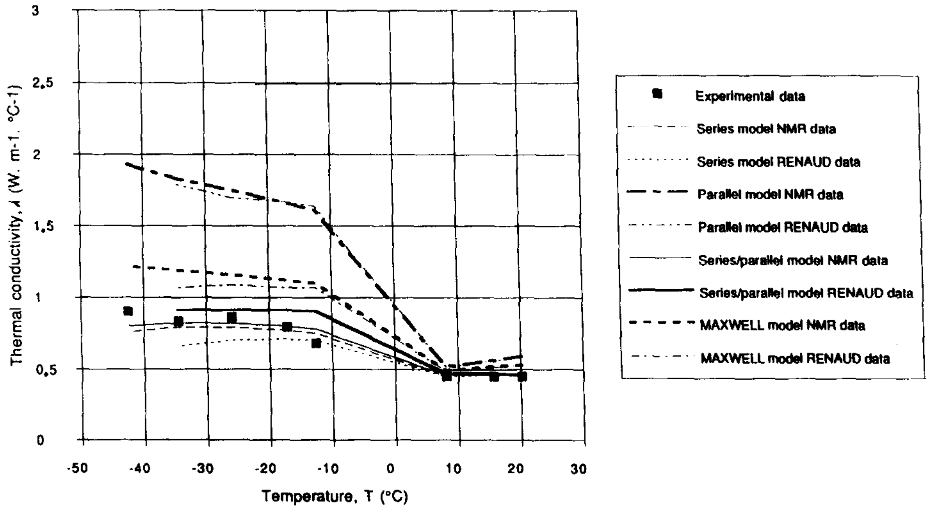

Fig. 20. Comparison of the thermal conductivity as a function of the temperature for the 30% ovalbumin gel.

CONCLUSIONS

The NMR technique allowed the measurement of the amount of different water states in frozen or unfrozen food gels. These data were used to model the heat capacity and the thermal conductivity of the same gels. This approach was interesting because the heat capacity prediction was improved in the frozen state.

Except for sucrose gels, the experimental determination of different fractions of water (bound water, ice, freezable water) allows a better prediction of thermal properties (heat capacity and thermal conductivity) of frozen gels.

The thermal conductivity modelling in the frozen state was more difficult due to the heterogeneity of the gels when the mixture froze. In spite of this heterogeneity in the frozen state, it could be interesting to complete this structure and texture characterisation using electronic microscopy or ultrasound.

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