Les propriétés rhéologiques des gels présure dépendent de la répartition des cations bivalents dans les micelles de caséine

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The rheological properties of rennet gels depend on the divalent cation distribution in the casein micelles

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Background

Rennet gel is a particle gel whose structure is dynamic. Its rheological properties depend on the strength and the number of bonds between particles (casein micelles) but also on their spatial distribution, i.e. their microstructure. From previous studies, it has been hypothesized that the micellar calcium phosphate (**MCP**) content of the casein micelles influences the gel viscoelastic character and its dynamic of rearrangements.

Low MCP content would result in more viscous gels that quickly rearrange, but this has been observed in a limited number of conditions. Divalent cations (Ca^{2+} and Mg^{2+}) also exist as free (**C.Free**) or as directly bound to casein residues (**C.Bound**), but they are seldom considered. **In this study, milk samples with various mineral composition were analyzed to determine how the mineral partition affects the rheological properties of rennet gels.**

Strategy

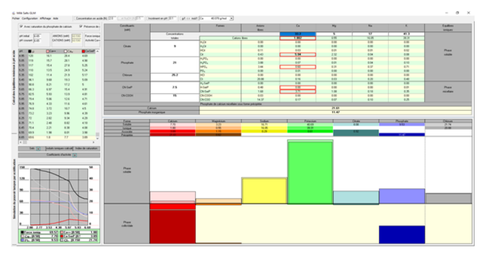
19 samples were prepared by adding different salts ($CaCl_2$, $MgCl_2$, Na_2HPO_4, $CitNa_3$) to milk or by varying the milk pH. Samples were gelled by rennet addition at 30°C and gel properties were assessed by small angle shear oscillatory rheology using a Couette geometry. A frequency sweep was initiated 120 min after rennet addition. Detailed mineral distribution was obtained by modelling salt equilibria from total ion concentrations using the Milk Salts GLM software [1].

No addition	2.5 $CaCl_2$	5 $CaCl_2$
6.65	6.60	6.50
10 $CaCl_2$	2.5 $CaCl_2$corr	5 $CaCl_2$corr
6.30	6.65	6.65
10 $CaCl_2$corr	HCl	HCl
6.65	6.60	6.50
HCl	HCl	2.5 Na_2HPO_4corr
6.30	6.00	6.65
5 Na_2HPO_4corr	10 Na_2HPO_4corr	2.5 $MgCl_2$
6.65	6.65	6.60
5 $MgCl_2$	10 $MgCl_2$	10 $MgCl_2$corr
6.50	6.40	6.65
2.5 $CitNa_3$corr		
6.65		

+ MCP / + C.Bound	+ MCP / - C.Bound
- MCP / + C.Bound	- MCP / - C.Bound

Salt additions to milk (mM) and corresponding milk pH

"corr" indicates that pH has been corrected after salt addition

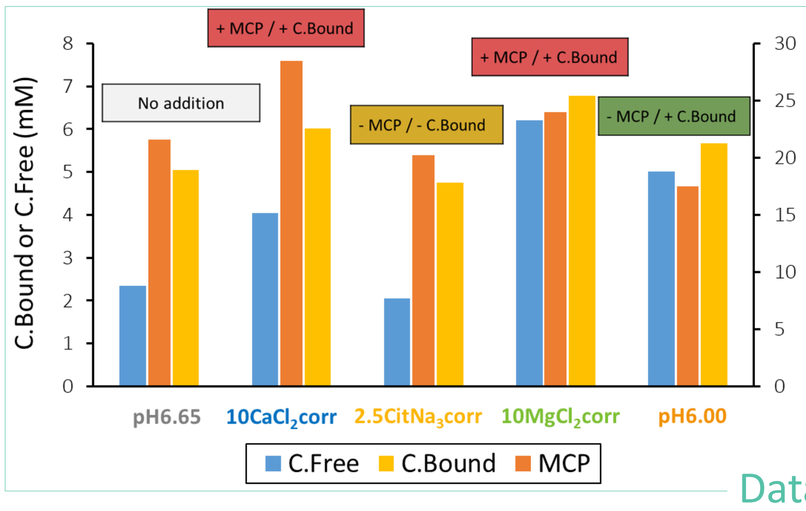


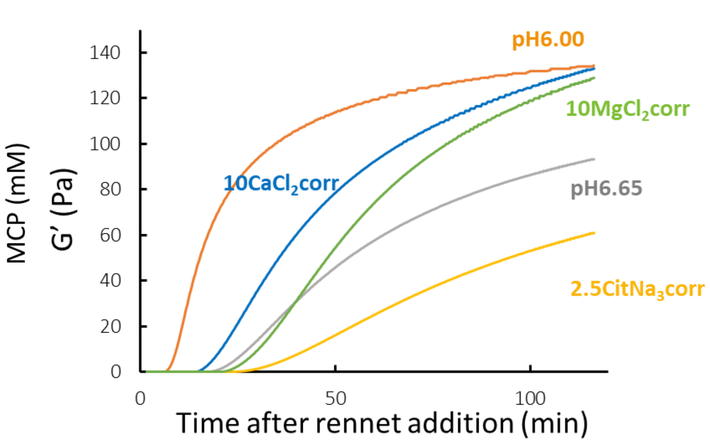
Modelling salt equilibria (from total ion concentrations)

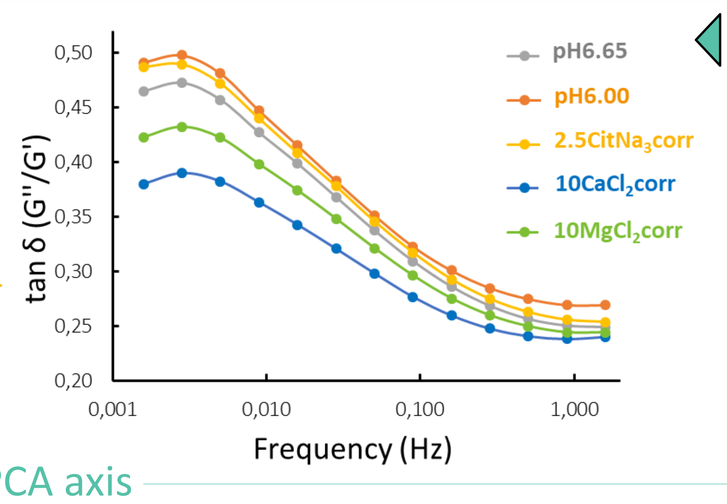
Gelation by rennet addition
Time sweep (120 min, ɣ=0.01, 0.1 Hz)
Frequency sweep (1.6 - 0.0016 Hz)

Experimental procedure

Results

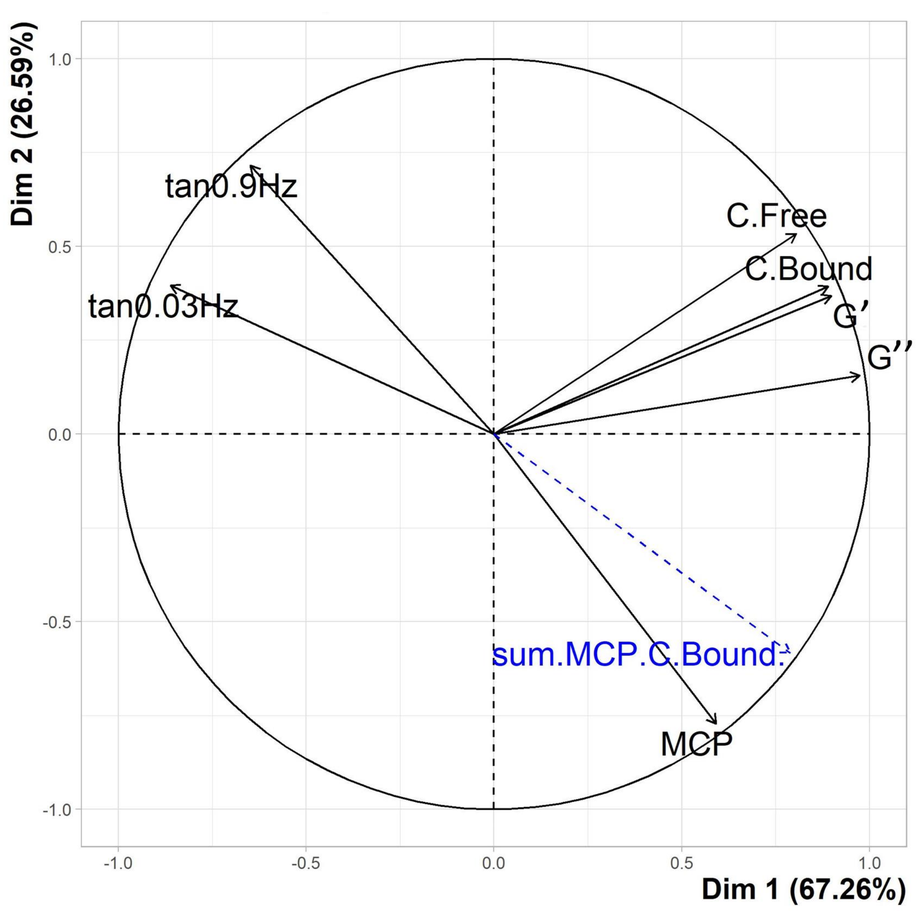






To reveal potential correlations between mineral distribution and rheological properties, the data set was simplified using principal component analysis (**PCA**).

Data of individuals highly contributing to PCA axis



- **tan0.9Hz**, **tan0.03Hz** = loss tangent at 0.9Hz and 0.3Hz (determined from the frequency sweep)
- **G'**, **G''** = moduli at 9h after coagulant addition (extrapolated at 120 min using the Scott-Blair model)
- **C.Free** = Ca_{ionic} + Mg_{ionic}
- **C.Bound** = (Ca + Mg) directly bound to caseins
- **MCP** = micellar calcium phosphate
- **sum.MCP.C.Bound** = $Ca_{colloidal}$ + $Mg_{colloidal}$ and was represented as supplementary data.

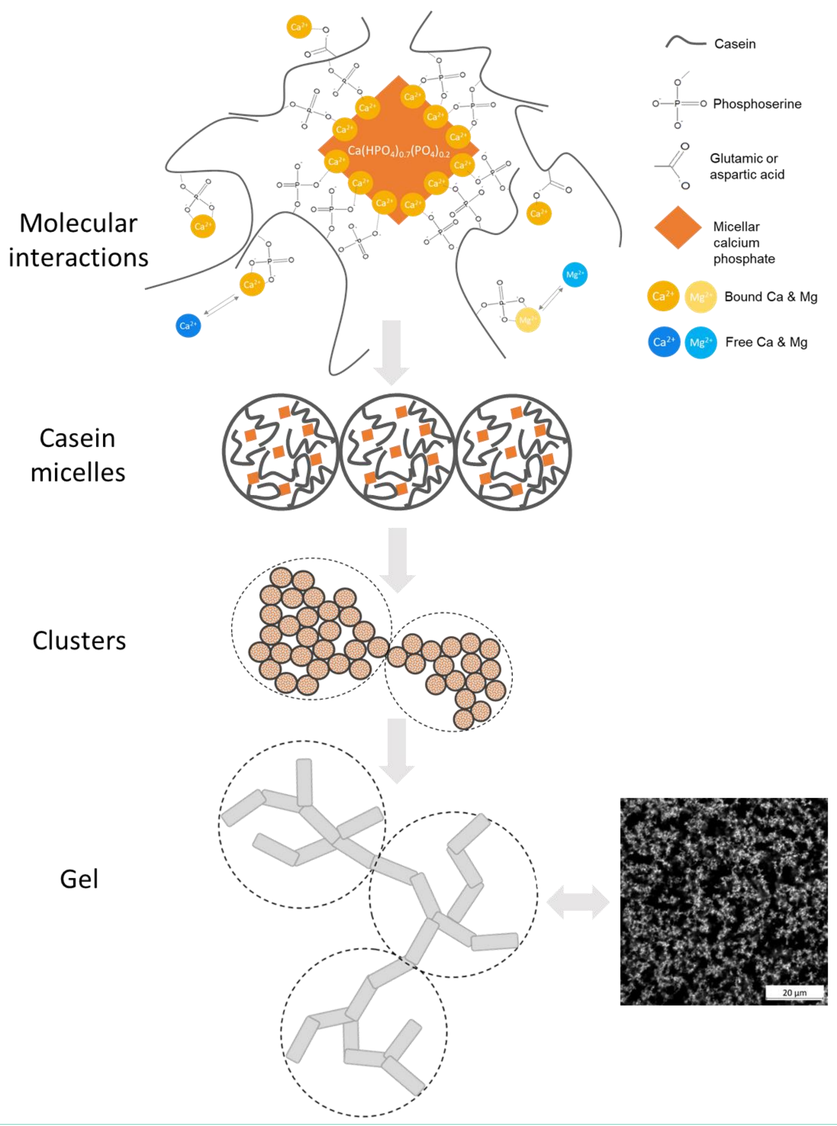
It has been suggested that the value of the moduli (G' and G'') depends on the number of bonds between casein micelles [2]. The correlation between C.Free, C.Bound, G' and G'' suggests that the direct binding of cations to caseins reduces electrostatic repulsions between casein micelles and promotes the creation of inter-micelle bonds. The MCP content was not correlated to the absolute value of the moduli but was anticorraleted to their ratio, the tanδ. Thus, the viscoelastic character of the gel depends on intra-micellar interactions that are enhanced by the presence of MCP.

It is not self evident through which mechanism and at which scale MCP affects the gel dynamics. We formulated 2 hypothesis :

-Bonds between MCP and caseins could directly participate to the gel rheological properties. Increased MCP content would increase the number of bonds with high relaxation time, giving the gel a more elastic character (decrease of tanδ).

-MCP could also affect the casein micelle mechanical properties (hardness). Harder or softer elementary particles could lead to different aptitudes to rearrangement and cluster shapes, leading to different gel structures.

Structural organization of rennet gel



[1] Mekmene, O., Y. Le Graët, and F. Gaucheron. 2009. A model for predicting salt equilibria in milk and mineral-enriched milks. Food Chem.
[2] Horne, D.S., and J.A. Lucey. 2017. Rennet-Induced Coagulation of Milk. Elsevier Inc.