STUDY OF WINE TARTARIC ACID SALT STABILIZATION BY ADDITION OF CARBOXYMETHYLCELLULOSE (CMC): COMPARISON WITH THE « PROTECTIVE COLLOIDS » EFFECT

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Abstract

Aims: Inhibition of potassium hydrogen tartrate (KHT) crystallization by carboxymethylcellulose (CMC) is tested in a model solution and in wines. Tartaric acid salt crystallization risk is assessed by computing the supersaturation, saturation temperature and excess KHT with respect to the saturation equilibrium using MEXTAR® (Mesure de l'EXces de TARtre) software.

Materials and results: Firstly, the time for crystals to appear was recorded by monitoring the conductivity in a model solution and in a wine, and the inhibition ratio was computed. At 11,5 °C, 0,5 mg.L^{-1} CMC inhibited KHT crystallization. The inhibitory effect increased exponentially with increasing CMC concentration and was several times greater than that of polysaccharides and polyphenols, the protective colloids in wine (Gerbaud *et al.*, 1997). At 2 °C, 30 mg.L^{-1} CMC had the same inhibitory effect than 10 mg.L^{-1} at 11.5°C.Secondly, 20 red and white wines were refrigerated for 3 weeks at -4 °C with CMC or metatartaric acid. Results show that the addition of 20 mg.L^{-1} CMC has an inhibitory effect at least equivalent to 100 mg.L^{-1} metatartaric acid. Furthermore, for 10 wines preheated for 8 days at 30 °C and then refrigerated for 2 months at 0 °C, 5 and 20 mg. L^{-1} CMC maintains its inhibitory efficiency, unlike metatartaric acid which is hydrolysed

Significance and impact of the study: The OIV-OENO 366-2009 and OIV-OENO 02/2008 resolutions recently authorized the use of CMC to prevent tartaric acid salt precipitation. With no impact on health, and stable under heating and in acid solution, CMC is an efficient candidate for tartaric stabilization. The optimal concentration of 20 mg.L^{-1} (2 g.hL^{-1}) should however be adapted to local wine storage conditions and KHT crystallization risk.

Key words: CMC, tartaric acid salts, crystallization, precipitation, additives

Résumé

Objectifs : L'effet de la carboxymethylcellulose (CMC) sur la cristallisation du bitartrate de potassium KHT est évalué dans une solution modèle et dans des vins. Le risque de cristallisation est mesuré par calcul de la sursaturation, de la température de saturation et du KHT en excès par rapport à l'équilibre de saturation avec le logiciel MEXTAR® (Mesure de l'EXces de TARtre).

Méthodes et résultats : Premièrement, le temps pour voir apparaître des cristaux est enregistré par suivi de la conductivité dans une solution modèle et dans un vin et le rapport d'inhibition est calculé. À 11,5 °C, 0,5 mg.L^{-1} de CMC inhibe la cristallisation du KHT. L'effet inhibiteur croît exponentiellement avec la concentration et est plusieurs fois supérieur à celui des colloïdes protecteurs du vin, polysaccharides et polyphénols (Gerbaud *et al.*, 1997). À 2 °C, 30 mg.L^{-1} de CMC est aussi efficace que 10 mg.L^{-1} à 11,5 °C. Puis, on démontre que 20 mg.L^{-1} of CMC est un inhibiteur équivalent à 100 mg.L^{-1} d'acide métatartrique dans 20 vins rouges et blancs, réfrigérés pendant 3 semaines à -4 °C. Enfin, dans 10 vins préchauffés 8 jours à 30 °C, puis réfrigérés 2 mois à 0 °C, l'acide métatartrique s'hydrolyse et perd son efficacité, mais pas à 5 et 20 mg.L^{-1} de CMC .

Signification et impact de l'étude : En accord avec les résolutions OIV-OENO 366-2009 et OIV-OENO 02/2008 autorisant la CMC pour prévenir les précipitations tartriques, ces résultats démontrent l'efficacité de cet additif sans effet sur la santé, stable à la chaleur et dans les conditions d'acidité des vins. La concentration efficace de 20 mg.L^{-1} (2 g.hL^{-1}) devra cependant être validée avec les conditions locales de conservation des vins et de leur risque de cristallisation.

Mots clés: CMC, sels tartriques, cristallisation, précipitation, additif

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TARTARIC STABILIZATION OVERVIEW

Potassium hydrogen tartrate (KHT) and calcium tartrate (CaT) crystallization is governed by the solid – liquid equilibrium of potassium and calcium ions with L(+)-tartaric acid. Consumers usually dont appreciate the presence of crystals in a wine bottle that can also cause excessive gushing (and loss of product) in sparkling wines. The crystallization of tartaric acid salts (tartrates) naturally occurs during alcoholic fermentation and continues during wine storage, either voluntarily by physical treatment or involuntarily after alkaline salt deacidification. Removing both cations and anions from the wine affects the pH, total acidity and buffering power of the wine (Devatine *et al.*, 2002 ; Blouin and Peynaud, 2005).

According to the crystallization theory, tartaric acid salts "crystallize" rather than "precipitate", because the rates of crystal nucleation and growth remain moderate with respect to truly precipitating salts for which very high local supersaturation makes crystal appearance almost immediate (Ratsimba, 1990 ; Gerbaud, 1996).

Compared to the solubility product of KHT and CaT, the elevated concentration in potassium and calcium, the main wine cations, and tartaric acid, the main wine anion (Blouin and Cruege, 2003 ; Taillandier and Bonnet, 2005) causes a supersaturation in both salts, and therefore a potential risk of crystallization in wine (Gerbaud, 1996). The saturation level of KHT and CaT decreases in time under cold storage conditions. The higher the supersaturation, the faster the crystallization rates, which is why mini-contact or freezing tartaric stabilization is recommended before winter (Blouin and Peynaud, 2005). Supersaturation is defined as a ratio of the salt ion composition in wine versus the salt ions compositions under saturation conditions. It can be computed by solving the thermodynamic equations describing the solid – liquid and dissociation equilibrium dependent on pH, taking into account the activity coefficients from the ionic strength, either approximately (Berg and Keefer, 1958 ; Usseglio-Tomasset *et al.*, 1992) or rigorously, accounting also for the tartaric acid salt complexes (Scollary, 1990 ; Cardwell *et al.*, 1991 ; Gerbaud, 1996). Rigorous KHT and CaT supersaturation calculations are routinely done with the help of software like MEXTAR (Blouin *et al.*, 1998). Alternatively, a wine is supersaturated if its temperature is below its saturation temperature, which can be computed (Blouin *et al.*, 1998) or measured by monitoring the conductivity directly (Würdig *et al.*, 1982 ; Maujean *et al.*, 1985, Garcia-Ruiz *et al.*, 1991) or indirectly with the Stabisat® apparatus (Ratsimba and Gaillard, 1988 ; Gaillard *et al.*, 1990 ; Favarel, 1991 ; Tusseau and Feneuil, 1992).

There are basically three methods for preventing tartaric acid salt crystallization in bottled wines :

1. Processes that induce salt precipitation before bottling by means of cooling the wine : stabulation process (Berg and Keefer, 1958 ; Brugirard and Rochard, 1991), « contact » process (Carles, 1892 ; Rhein, 1977 ; Müller-Spath, 1977, Rhein and Neradt, 1979 ; Blouin *et al.*, 1979) and various continuous processes (Ratsimba, 1990) ;

2. Processes that selectively remove excess potassium and/or calcium ions : ion exchange resin process (Clutton, 1974) or electrodialysis (Moutounet *et al.*, 1991 ; Moutounet *et al.*, 1994) ;

3. Processes that use crystallization inhibitors, such as metatartaric acid (Peynaud and Guimberteau, 1961), yeast mannoproteins (Lubbers *et al.*, 1993 ; Moine and Dubourdieu, 1995 ; Moine-Ledoux *et al.*, 1997 ; Moine-Ledoux and Dubourdieu, 2002) and at last carboxymethylcellulose gums (CMC) that we are concerned with in this study (Wucherpfennig *et al.*, 1984 ; Crachereau *et al.*, 2001 ; Tusseau, 2009 ; Motta *et al.*, 2009).

As pointed out at a recent technical workshop on wine tartaric stabilization (Favarel, 2009), all processes are worth investigating when facing a risk of tartaric acid salt crystallization, even those having drawbacks. For example, cooling processes are expensive to set up and operate and may be partly inefficient if the wine supersaturation is too low or in red wine where natural colloids inhibit crystal nucleation and growth. Electrodialysis is relatively cheap to operate but requires expensive equipment and may induce pH increase that is sometimes not wanted. Metatartaric acid is extremely efficient until it hydrolyses naturally after a few months or after a few days under heating, releasing then tartaric acid that reinforces supersaturation. Yeast mannoproteins are efficient inhibitors at a concentration of 200 $mg.L^{-1}$ in some wines. But for highly saturated wines where a higher concentration is needed to achieve the same inhibitory effect, mannoprotein flocculation may occur that counteracts the expected effect.

CMC effect in model solutions and in wines was studied in laboratory conditions from 1993 to 1998 as part of a PhD project (Gerbaud, 1996) and in subsequent years at the Gironde Chamber of Agriculture (CA33) in Blanquefort, in collaboration with the « Laboratoire de Génie Chimique » UMR CNRS 5503 in Toulouse. Having obtained a 3-year experimentation agreement under the article 26 of the EEC n° 822/27 regulation, the CA33 studied the effect of CMC on large volumes of wine from various French wine production areas. The results of this 3-year study were presented at the XXVth World Congress of Vine and Wine in Paris, June 2000 and published by

Crachereau *et al.* (2001). Crachereau *et al.* noted that CMC has a remarkable effect on preventing tartaric precipitation. The laboratory results obtained between 1993 and 1998 were not published in the scientific literature. The present article aims at publishing these data, in the context of the recent « Office International des Vins » resolutions, OIV-OENO 366-2009 (monography on carboxymethylcelluloses (cellulose gums)) and OIV-OENO 02/2008 (Wine – Treatment using cellulose gum (Carboxymethylcellulose)) that specifies the use of CMC for wine tartaric stabilization. In 2001, a preliminary study on CMC by the CA33 was transmitted to the OIV and recalled when these resolutions were issued.

After a short introduction on the methods and tools that allow quantification of the inhibitory effect of an additive versus tartaric acid salt precipitation, the study conditions, the wines and the solutions are presented. The efficiency of CMC is assessed in model solution by recording the induction time and is studied in wine by observing the presence or absence of crystals after several weeks of cold storage at -4 °C. Furthermore, CMC is compared to metatartaric acid, in particular to evaluate its ability to withstand heat while maintaining its protective effect.

QUANTIFYING THE EFFECT OF « PROTECTIVE COLLOIDS » AND OTHER ADDITIVES ON TARTARIC PRECIPITATIONS

Tartaric stabilization processes using additives mimic the « protective colloïds » effect. Indeed, wines, red ones in particular, have been suspected for many years to prevent or slow tartaric salt crystal appearance (nucleation) and to lower the efficiency of cold tartaric stabilization (Carles, 1892 ; Berg, 1953 ; Balakian and Berg, 1968 ; Brugirard, 1979). Later, the inhibitory effect of wine colloids was confirmed (Wücherpfennig *et al.*, 1984 ; Maujean *et al.*, 1985 ; Maujean *et al.*, 1986 ; Rodriguez-Clemente and Correa-Gorospe, 1988 ; Lubbers *et al.*, 1993 ; Moine and Dubourdieu, 1995 ; Gerbaud *et al.*, 1997 ; Dubourdieu and Moine, 1997 ; Moine-Ledoux *et al.*, 1997 ; Moine-Ledoux et Dubourdieu, 2002) and the polysaccharides and polyphenols involved were identified (Gerbaud *et al.*, 1997 ; Vernhet *et al.*, 1999a ; Vernhet *et al.*, 1999b ; Doco *et al.*, 2000).

The effect of an additive on crystallization depends on its concentration at a given temperature (Mullin, 1993). Among the additives cited above, only metatartaric acid is considered as a complete inhibitor of tartaric salt crystal nucleation and growth, until its hydrolysis occurs. Other additives merely slow crystal appearance and possibly their growth.

1. Evaluating the crystallization risk by computing the supersaturation

Supersaturation (*S*) is the ratio of the wine state versus the saturation state, which is expressed by the thermodynamic solubility product. For KHT, *S* equals :

$$S = \frac{\sqrt{m_{K^+} \cdot m_{HT^-} \cdot \gamma^2_{\pm,KHT}}}{\sqrt{K^*_{solubility}}} \qquad (1)$$

where

- $\gamma_{\pm KHT}$: mean activity coefficient of potassium hydrogen tartrate, which varies with ionic strength and temperature,

- m_i : molality of free (not involved in complexes) ion i (in mol.kg^{-1}),

- $K^*_{solubility}$: thermodynamic solubility product that, according to solid – liquid equilibrium thermodynamics varies only with temperature, pressure and alcohol content (% v/v) for a given reference state (taken here as atmostpheric pressure).

By definition, the saturation temperature of a wine is the temperature at which $S = 1$.

The distribution of ions in solution, m_i, is computed by solving the solid – liquid and the dissociation equilibrium together with the electroneutrality equation. It should also consider the complexation equilibrium of approximately 12 % of potassium and 10 % of tartaric acid in wines (Gerbaud, 1996) and that concerning calcium (Scollary, 1990 ; Cardwell *et al.*, 1991). Complexes sequester free ions that could participate in crystallization. M_i depends on the pH and the ion distribution through the ionic strength *I*. As pointed out by Berg and Keefer (1958) and Usseglio-Tomasset (1995), the mean ionic strength *I* in wine is 0.04 mol/kg, making wine a diluted solution like any other electrolyte solution for which simple Debye-Hückel equation can be used to compute activity coefficients (Zemaitis *et al.*, 1986). Solving the Debye-Hückel equation with $I = 0.04$ mol/kg gives $\gamma_{\pm KHT} = 0.83$ at 25 °C. MEXTAR® solves all the rigorous equilibrium equations for hydroalcoholic solutions and wines between 8 and 16 % v/v and provides an accurate value for the pH and the saturation temperature of tartaric acid salts (Blouin *et al.*, 1998 ; Devatine *et al.*, 2002 ; Gerbaud *et al.*, 2003). Neglecting the complexes and the impact of ionic strength on the activity coefficients leads to an overestimatation of supersaturation by 10 % and an underestimation of pH by 0.1 to 0.2 pH units between pH 3 and 4 (Gerbaud, 1996).

At ambient temperature before the stabilization treatment, most of the wines are supersaturated : their saturation temperature is higher than the ambient

temperature and they may crystallize (Gerbaud, 1996). When temperature decreases or when the percentage of alcohol (v/v) increases, tartaric acid salt solubility decreases and thus supersaturation increases along with the risk of tartaric precipitation.

2. Effect of additives on crystal appearance

By monitoring the conductivity under constant temperature, the induction time, that is the time needed for crystals to appear, can be recorded. The inhibition ratio (*IR*) is defined as the ratio of the induction time with and without additive in the same solution and at the same temperature (Gerbaud, 1996). This is the best experimental protocol to compare additives because it records primary nucleation, which is the main phenomenon responsible for crystal appearance in bottled wines under normal storage conditions.

Other indirect measurements of the additive effect have been used : the mini-contact test records secondary nucleation induced at the surface of crystals added to the wine. Secondary nucleation is faster than primary nucleation and may occur on particles in the wine or imperfections (scratches and residues) on the bottle. Coupled with conductivity monitoring, the mini-contact test was used to prove the inhibitory effect of CMC (Tusseau, 2009 ; Motta *et al.*, 2009). Monitoring the conductivity drop during crystal growth enabled Maujean *et al.* (1986) to assess the effect of inhibitors on growth and they found that metatartaric acid completely blocked crystal growth. The refrigeration test detects the presence or absence of crystals in wine after keeping it under high supersaturation conditions, for instance 3 weeks at -4 °C. But it enables, at best, to assess how inefficient is an additive.

3. Review of tartaric acid salt precipitation inhibition by « protective colloids »

Gerbaud *et al.* (1997) studied the effect of wine polysaccharides, in particular type I and II rhamnogalacturonans (RG-I and RG-II) and arabinogalactan-protein (AGP_0, AGP_2, AGP_3, AGP_4), wine mannoproteins (MP_0-a, MP_0-b, MP_0-c, MP_0 total, MP_1, MP_2), wine polyphenols, and mannoproteins extracted from yeast cells (MP_{lev} et MP_{lev}-a), by recording the induction time in a model solution (12 % v/v alcohol, 2.42 g.L^{-1} KHT, 2 g.L^{-1} K_2SO_4, pH = 3.77, T_{sat} = 27 °C) equivalent to 1.93 g.L^{-1} of tartaric acid and 1.39 g.L^{-1} of potassium. The crystallization risk was evaluated by computing its supersaturation, namely S = 1.67 at T = 11.5 °C, and by measuring a mean induction time without additive equal to tind 1 h 20 min ± 15 minutes (Gerbaud, 1996).

Under S = 1.67 at T = 11.5 °C, polyphenols are the best inhibitor, with an inhibition ratio of *IR* = 5 at a concentration of 2,000 mg.L^{-1} and *IR* = 180 at 4,000 mg.L^{-1}. However, such polyphenol concentration cannot be added to a wine without signficant modification of its organoleptic features. RG-II favors crystal nucleation up to 100 mg.L^{-1} but inhibits it above that concentration with *IR*~1.2 to 1.4. RG-I, AGP_0, AGP_2, AGP_3 and AGP_4 are also weak inhibitors of crystal nucleation with R~2 to 3 at 20 mg.L^{-1}. Regarding mannoproteins, the fractions MP_0-a, MP_0-b, MP_0-c, MP_0 total, MP_1 and MP_2 found in wine are slightly inhibitory with *IR*~2 at 20 mg.L^{-1}. Yeast cell mannoproteins MP_{lev} and MP_{lev}-a are much better inhibitors with *IR* > 150 at 150 mg.L^{-1}. When temperature is lowered to 2 °C (S = 2.38), the inhibitory effect of MP_{lev} and MP_{lev}-a is lowered as *IR* = 30 at 530 mg.L^{-1}.

According to Gerbaud *et al.* (1997), those « protective colloids » effects are coherent with the commonly acknowledged behavior of white and red wines. White wines have low polyphenol content and are rich in RG-II, with concentrations between 20 and 50 mg.L^{-1} that correspond to concentrations where RG-II is a promoter of crystal nucleation. Red wines contain all the studied colloids, in particular polyphenols in concentrations between 1,000 and 4,000 mg.L^{-1} and RG-II in concentrations above 100 mg.L^{-1}, within the range where an inhibitory effect is observed on tartaric acid salt precipitation.

USE OF CMC IN WINE

1. Features of the commercial CMCs used in this study

The commercial CMCs used in this study are the same as those used by Crachereau *et al.* (2001). They match the features authorized by the O.I.V. in the OIV-OENO 366-2009 regulation, which describes the CMC to be used in wine for tartaric stabilization. CMC are polymers of cellulose rings substituted by carboxymethyl organic acid chemical groups often saturated by sodium. Pure CMC pKa is around 4.3 and under wine pH conditions, about 20 % of the carboxymethyl groups carry negative charges in solution.

- CMC BLANOSE 7LF (Aqualon – France) has a low substitution degree (SD = 0.65 to 0.90) and a low polymerization degree, which leads to a moderate viscosity between 25 and 50 mPa for a 2 % solution at 25 °C. Of food quality grade, its purity is greater than 99.5 % (incl. less than 0.4 % of sodium glycolate). Its pH for a 2 % solution is close to 7.

- CMC WALOCEL CRT 10 g (Wolff Walsrode – Germany), viscosity 10 mPa at 20 °C, 2 % solution.

- CMC WALOCEL CRT 5 g (Wolff Walsrode - Germany), viscosity 5 mPa at 20 °C, 2 % solution.

Commercial CMC is a powder soluble in hot water, with constant gentle mixing, leading to a slightly viscous solution. As mentionned by Tusseau (2009), a complete dissolution of CMC is necessary before incorporation in wine. So a 20 - 40 $g.L^{-1}$ CMC solution was prepared, limiting the introduction of water to 0.1 – 0.2 L per hL of wine for wine treatment with 20 $mg.L^{-1}$ of CMC.

2. Studied solutions and wines

a. Model solution

The model solution studied is the same as the one used to study the effect of polysaccharides and polyphenols on wine tartaric stabilization (Gerbaud, 1996 ; Gerbaud *et al.*, 1997) : 12 % v/v alcohol, 2.42 $g.L^{-1}$ KHT, 2 $g.L^{-1}$ K_2SO_4, pH = 3.77. It is equivalent to 1.93 $g.L^{-1}$ of tartaric acid and 1.39 $g.L^{-1}$ of potassium. Rigorously computed with the help of MEXTAR® (Blouin *et al.*, 1998 ; Devatine *et al.*, 2002 ; Gerbaud *et al.*, 2003), its saturation temperature equals T_{sat} = 27 °C and the crystallisation risk at 11.5 °C is evaluated by the supersaturation equal to S = 1.67.

b. Wines

Twenty-one wines were studied :

- 20 wines during the refrigeration tests :
. From Bordeaux area : 9 dry white wines, 2 sweet wines, 10 red wines ;
. From Côtes du Rhône AOC : 1 white wine and 1 red wine ;
. From Nantes area : 2 white wines ;

- 1 red wine, noted VR4, during the induction time tests.

All wines were unstabilized (no filtration, no fining). Table 1 displays the chemical analysis of the wines. Knowledge of pH, total acidity, tartaric acid (TarAc), malic acid (MalAc), and potassium concentrations enables to assess KHT crystallization risk (supersaturation, saturation temperature and maximum KHT crystal amount (excess amount) recoverable at -4 °C by using MEXTAR® software). Knowledge of malic and lactic (Lac) acids is not mandatory but improves the accuracy of the prediction (Blouin *et al.*, 1998).

Table 1 shows that 10 wines (1 white and 9 reds) are supersaturated at 20 °C ($S > 1$; $T_{sat} > 20$ °C) and that all wines are supersaturated at -4 °C ($1.69 < S < 2.95$).

Wine VR4 was supplemented with 1.5 $g.L^{-1}$ of KHT in order to increase its tartaric acid salt unstability. As a result, it showed the highest crystallization risk of all studied wines : KHT addition led to S = 1.5 at 20 °C and S = 3.5 at -4 °C, along with an increase of tartaric acid and potassium and of total acidity. The KHT excess amount increased by 1.5 $g.L^{-1}$.

The combination of many factors, such as ion distribution, pH, % v/v, etc. is responsible for the distribution of the supersaturation S values for the wines displayed in table 1.

INHIBITION RATIO MEASUREMENT IN MODEL SOLUTIONS AND IN A RED WINE

The induction time was recorded in 150 ml of solution, either model solution or wine VR4, under continuous magnetic stirring and constant temperature, with and without additive in order to compute the inhibition ratio.

Without additive at 11.5 °C (S = 1.67), the induction time of the model solution equals 1 h 20 min ± 15 minutes, averaged over 38 measurements. Such a model solution has no protective colloids and the KHT crystallization is much faster than in a red wine at the same supersaturation (Gerbaud, 1996).

Without additive, wine VR4 + 1.5 $g.L^{-1}$ of KHT shows a mean induction time equal to 1 h 15 min at 11.5 °C (S = 2.02).

1. Effect of CMC in a model solution

The inhibition ratio values for the model solution are presented in table 2 (S = 1.67 ; T = 11.5 °C) and table 3 (S = 2.38 ; T = 2 °C).

All three CMCs exhibit an inhibitory effect that increases with increasing CMC concentration, starting at concentration as low as 0.5 $mg.L^{-1}$ (0.05 $g.hL^{-1}$) ! Compared to results obtained for polyphenols and polysaccharides on the same model solution under the same conditions (see section II.3), CMC is a much better inhibitor, reaching equivalent or higher inhibition ratio at concentrations 10 times lower than polysaccharides and 50 to 200 times lower than polyphenols.

When the crystallization risk is increased through the supersaturation by decreasing the temperature to 2 °C, CMC still has a strong inhibitory effect, but concentrations 3 to 5 times higher than at 11.5 °C are needed to reach the same inhibition ratio.

2. Effect of CMC in a highly unstable wine at 11.5 °C

Addition of 1.5 $g.L^{-1}$ of KHT to wine VR4 is equivalent to a wine with 1.3 $g.L^{-1}$ of potassium and 2.8 $g.L^{-1}$ of tartaric acid. The resulting wine is the most

Table 1 - Chemical analysis of wines

Wine n°		Type	Origin	Alcohol	Total Acidity	pH	Free SO_2	SO_2 Total	K^+	TarAc	MalAc	LacAc	Supersaturation (S) *		T_{sat}	KHT excess amount at -4°C **
													at 20°C	at -4°C		
				% v/v	$g.L^{-1}$		$mg.L^{-1}$	$mg.L^{-1}$	$mg.L^{-1}$	$g.L^{-1}$	$g.L^{-1}$	$g.L^{-1}$			°C	$g.L^{-1}$
1	899	Dry white	Muscadet	11.6	4.3	3.23	8	38	700	2.3	3.9	0.18	0.92	2.20	18.0	1.72
2	900	Sweet white	Bordeaux 1	13.3	3.9	3.49	76	296	1350	0.8	3.0	0.31	0.80	1.81	14.2	0.77
3	901	Dry white	Gros Plant	10.5	5.7	2.97	12	38	400	4.7	4.5	0.15	0.70	1.69	10.0	1.03
4	902	Dry white	C. du Rhône 1	12.3	4.7	3.26	12	119	950	3.0	4.0	0.19	1.23	2.92	25.6	2.74
5	903	Sweet white	Bordeaux 2	11.5	4.5	3.18	29	178	800	1.9	3.6	0.16	0.87	2.06	16.1	1.57
6	904	Dry white	Bordeaux 3	11.4	5.0	3.24	15	63	750	2.3	5.0	0.14	0.93	2.24	18.1	1.78
7	905	Dry white	Bordeaux 4	11.3	4.4	3.23	27	135	850	2.0	4.1	0.28	0.94	2.28	18.5	1.74
8	906	Dry white	Bordeaux 5	12.0	6.0	3.03	9	58	600	4.3	4.8	0.19	0.83	1.94	14.8	1.41
9	907	Dry white	Bordeaux 6	12.1	4.8	3.23	15	113	750	2.4	4.8	0.18	0.95	2.23	18.7	1.79
10	908	Dry white	Bordeaux 7	11.6	5.1	3.09	15	70	600	3.0	4.7	0.19	0.87	2.07	16.3	1.61
11	909	Dry white	Blayais 1	11.6	4.4	3.31	10	123	950	1.8	4.2	0.57	0.97	2.32	19.4	1.68
12	954	Red	Bordeaux 8	12.5	3.1	3.67	15	39	1400	1.6	0.1	2.13	1.15	2.73	23.6	1.71
13	955	Red	Medoc 1	12.1	3.2	3.63	19	64	1300	2.0	0.1	2.15	1.23	2.95	25.6	2.16
14	956	Red	Bordeaux 9	11.3	3.7	3.64	34	110	1250	1.5	0.0	2.40	1.03	2.52	20.7	1.55
15	957	Red	Bordeaux 10	12.1	3.1	3.61	20	62	1200	1.9	0.1	2.16	1.17	2.78	24.0	2.01
16	958	Red	Medoc 2	12.4	3.2	3.67	39	91	1350	1.8	0.1	2.04	1.20	2.86	24.7	1.94
17	959	Red	Bordeaux 11	11.7	3.4	3.63	20	107	1400	1.7	0.6	2.24	1.15	2.79	23.8	1.88
18	960	Red	Blayais 2	11.9	3.1	3.63	26	80	1300	1.4	0.1	2.06	1.03	2.48	20.7	1.5
19	961	Red	C. du Rhône 2	12.0	3.2	3.71	18	68	1400	1.5	0.0	2.46	1.10	2.65	22.4	1.59
20	962	Red	Bordeaux 12	12.0	4.3	3.60	30	121	1350	1.2	0.2	2.03	0.97	2.32	19.5	1.21
21	VR4	Red	Bordeaux 1990	12.9	2.9	3.63	22	57	1014	1.6	0.3	2.00	1.04	2.47	20.8	1.56
	VR4	+1.5 $g.L^{-1}$ KHT		12.9	3.3	3.61	22	57	1325	2.8	0.3	2.00	1.51	3.50	30.5	3.06

Ac: acid; Mal: malic; Tar: tartaric; Lac: lactic
* S, Tsat computed with MEXTAR.
** computed with MEXTAR to reach saturation at -4 °C

Table 2 - Inhibition ratio in a model solution 12 % v/v (S = 1.67 ; T = 11.5 °C)

Model solution	$C_{additive}$ (mg.L^{-1})	0.5	1	2	6	10
CMC Blanose7LF	Inhibition ratio	1.56	1.70	2.23		> 45
	Crystal occurrence*	+	+	+		0
CMC Walocel CRT 5G	Inhibition ratio				> 28	
	Crystal occurrence*				0	
CMC Walocel CRT 10G	Inhibition ratio				> 37	
	Crystal occurrence*				0	

* +: crystal appearance; 0: experience stopped before crystal appearance.

Table 3 - Inhibition ratio in a model solution 12 % v/v (S = 2.38 ; T = 2 °C)

Model solution	$C_{additive}$ (mg.L^{-1})	8	30
CMC Blanose7LF	Inhibition ratio	1.15	23.32
	Crystal occurrence*	+	+

* +: crystal appearance.

Table 4 - Inhibition ratio of wine VR4 added with 1.5 g.L^{-1} of KHT (S = 2.02 ; T = 11.5 °C)

Wine VR4 + 1.5 g.L^{-1} KHT	$C_{additive}$ (mg.L^{-1})	2.5	10
CMC Blanose7LF	Inhibition ratio	> 40	> 65
	Crystal occurrence*	0	0

* 0: experience stopped before crystal appearance.

unstable of all wines studied, with a saturation temperature equal to 30.5 °C (table 1).

Inhibition ratios at 11.5 °C (S = 2.02) are presented in table 4.

Again, CMC displays a strong inhibitory effect at 2.5 mg.L^{-1}, increasing in parallel with increasing CMC concentrations. The effect is seemingly stronger than in model solutions, likely due to the protective effect of natural polyphenols and polysaccharides already mentionned.

Moreover, wine VR4 has also 0.1 g.L^{-1} of calcium. With the addition of 1.5 g.L^{-1} of KHT, MEXTAR® software predicts that the resulting wine is undersaturated for calcium tartrate at 20 °C (S_{CaT} = 0.94) and slightly supersaturated at 11.5 °C (S_{CaT} = 1.21). However, no calcium salt precipitates were detected. It is acknowledged that CaT precipitates after KHT, and that KHT precipitation decreases the calcium salt crystallization risk (Ratsimba, 1990).

EFFECT OF CMC IN WINE AFTER REFRIGERATION TEST

Recording of the presence or absence of crystals after refrigeration for 3 weeks at -4 °C was performed in the cellar of the Gironde Chamber of Agriculture in Blanquefort, on 20 wines described in table 1. For each experimental condition, results are the average of three bottles.

1. Refrigeration test

Following the same procedure than above, wines treated with either CMC or metatartaric acid were kept at -4 °C for 3 weeks and crystal occurrence was checked. Table 5 presents the results and recalls the supersaturation values computed with MEXTAR®.

Tartaric acid and potassium analyses done on blank samples (without additives) that displayed crystals showed no significative differences among the wines, because the crystal amount corresponded to concentration differences that were less than the common chemical analysis standard deviation (according to OIV/EEC regulations).

Table 5 - Tartaric stabilization of wine by addition of CMC Blanose 7LF or metatartaric acid after refrigeration at -4 °C for 3 weeks

Wine n°	Wine (W)hite or (R)ed	Supersaturation		Blank sample	+ 5 mg.L^{-1} CMC BLANOSE 7LF	+ 20 mg.L^{-1} CMC BLANOSE 7LF	+ 100 mg.L^{-1} Metatartaric acid
		at 20°C	at -4°C	-4°C during 3 weeks			
899	Muscadet (W)	0.92	2.20	++	0	0	0
900	Cadillac (W)	0.80	1.81	++++	0	0	0
901	Gros plant (W)	0.70	1.69	++	0	0	0
902	Côtes du Rhône (W)	1.23	2.92	++++	0	0	0
903	Soussac 1 (W)	0.87	2.06	+	0	0	0
904	Soussac 2 (W)	0.93	2.24	++	0	0	0
905	Grezillac (W)	0.94	2.28	+	0	0	0
906	600 n°9 (W)	0.83	1.94	++++	0	0	0
907	604 Sauvignon (W)	0.95	2.23	+++	0	0	0
908	604 Muscadelle (W)	0.87	2.07	++	0	0	0
909	Blaye (W)	0.97	2.32	++	0	0	0
954	Coutras (R)	1.15	2.73	++	0	0	0
955	Pauillac Ht Medoc (R)	1.23	2.95	+++	0	0	0
956	604 CS temoin (R)	1.03	2.52	+++	0	0	0
957	Grezillac temoin (R)	1.17	2.78	+++	0	0	0
958	Pauillac (R)	1.20	2.86	+++	0	0	0
959	Cadillac temoin (R)	1.15	2.79	+++	0	0	0
960	Blaye temoin (R)	1.03	2.48	+++	0	0	0
961	Côtes du Rhône (R)	1.10	2.65	++	0	0	0
962	604 CF temoin (R)	0.97	2.32	+	0	0	0

Crystal amount: 0 none; + to ++++ increasing amount

Table 5 shows that all blank samples exhibit various crystal amounts (recorded visually). In spite of the qualitative feature of a visual observation, the crystal amount seems correlated with supersaturation for red wines, but not for white wines.

None of the wines treated with additives, 5 or 20 mg.L^{-1} CMC or 100 mg.L^{-1} metatartaric acid, show crystals. We conclude that after 3 weeks of cooling at -4 °C, 5 mg.L^{-1} CMC has the same inhibitory efficiency as 100 mg.L^{-1} metatartaric acid.

2. Heating followed by refrigeration test

a. Model solution tests

In order to evaluate the stability of CMC under heating, a clear drawback of metatartaric acid, the model solution was added with 20 mg.L^{-1} CMC or with 100 mg.L^{-1} metatartaric acid, heated for 2 heures at 40 °C, then cooled at 11 °C and agitated for 100 heures.

Table 6 shows that the metatartaric acid efficiency is destroyed by heating which induces hydrolysis of tartaric acid, thus reinforcing the wine unstability.

b. Wine tests

Ten wines were kept at 30 °C for 8 days, then refrigerated at 0 °C for 2 months. Results are reported in table 7.

Again, the results show that 100 mg.L^{-1} metatartaric acid looses its inhibitory efficiency as 4 cases out of 10 exhibit crystals. At 5 mg.L^{-1}, CMC does not prevent the presence of crystals in 5 cases out of 10, including 2 cases with atypical star-like crystals. At 20 mg.L^{-1} CMC, only 1 case exhibits KHT crystal deposit and the same

Table 6 - Heating impact on metatartaric acid and CMC BLANOSE 7LF effect on tartaric precipitation in model solution

Model solution	$C_{additive}$ (mg.L^{-1})	Heating	Cooling	Crystals
CMC Blanose7LF	20	Ambient temperature	11°C, 100 hrs	0
CMC Blanose7LF	20	2 hrs at 40°C	11°C, 100 hrs	0
Metatartaric acid	100	Ambient temperature	11°C, 100 hrs	0
Metatartaric acid	100	2 hrs at 40°C	11°C, 100 hrs	++++

Table 7 - Heat impact on metatartaric acid and CMC BLANOSE 7LF effect on tartaric precipitation in wines

Wine n°	**Wine** (W)hite or (R)ed	+ 5 mg.L^{-1} CMC BLANOSE 7LF	+ 20 mg.L^{-1} CMC BLANOSE 7LF	+ 100 mg.L^{-1} metatartaric acid
		+ 8 days at 30°C followed by 2 months at 0°C		
900	Cadillac (W)	0	0	0
901	Gros plant (W)	+	0	++
902	Côtes du Rhône (W)	0	0	(+)
906	600 n°9 (W)	0	0	0
907	604 Sauvignon (W)	+	(+)	++
954	Coutras (R)	++	N.A.	+
958	Pauillac (R)	+?	+?	0
959	Cadillac temoin (R)	0	0	0
960	Blaye temoin (R)	+?	+?	0
961	Côtes du Rhône (R)	0	0	0

Crystal amount : 0 none ; + to ++++ increasing amount
(+) suspected. +?: peculiar star-like crystals.

2 "+?" cases as with 5 mg.L^{-1} exhibit atypical star-like crystals.

The star-like crystals are distinct from the usual rhomboedral shape of KHT crystals (Rodriguez-Clemente and Correa-Gorospe, 1988 ; Gerbaud, 1996). They could well be crystals of another chemical substance but that was not further investigated during the tests. Gerbaud (1996) and Crachereau *et al.* (2001) investigated the effect of CMC on KHT crystal shapes and noted that CMC flattened the crystals and slowed the growth by a factor 7. More specifically, CMC slowed the growth of the main crystallographic face (010), hinting at a strong interaction between this face, that displays overall electropositive charges due to potassium ions, and CMC that is negatively charged under wine pH conditions. Thus, CMC competes with K+ and HT- ions in solution, preventing their attachement to the crystal faces (figure 1). The (130) and (101) crystallographic faces also disappear with CMC, because their relative growth rate becomes too large compared to the growth of the (010) face.

Haziness was observed in some wines, that corresponds to non crystalline precipitations usually observed in unstabilized (filtration, fining) wines, such as those used, that are kept under low temperature for long periods.

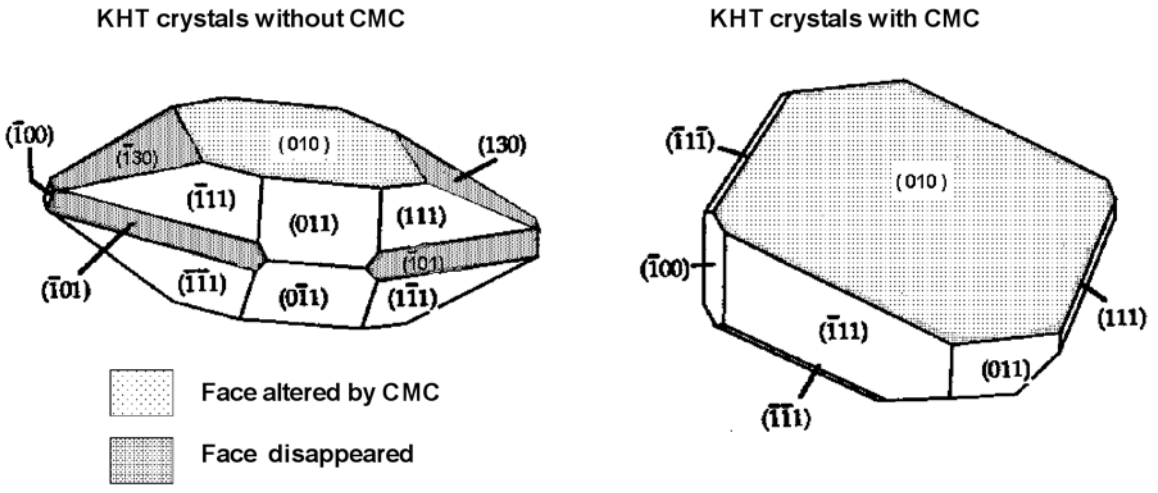

Figure 1 - Sketch of potassium hydrogen tartrate crystals with and without CMC (Gerbaud, 1996).

DISCUSSION

The results are in agreement with those reported by Wucherpfennig *et al.* (1984), Crachereau *et al.* (2001) and Motta *et al.* (2009). They evidence the inhibitory effect of CMC at very low concentrations, several times lower that those of other inhibitors like protective colloids and metatartaric acid, in a model solution and in a selection of wines.

More specifically, 20 mg.L^{-1} CMC has an inhibitory effect equivalent to 100 mg.L^{-1} metatartaric acid, also withstanding heating, which is not the case of metatartaric acid. CMC is not a complete inhibitor but its efficiency increases with concentration, without showing any limiting efficiency.

CONCLUSION

Recording the induction time by monitoring the conductivity in a model solution and in a wine has enabled to compute the inhibition ratio and to compare the inhibitory effect of CMC on tartaric acid salt precipitation with that of natural protective colloids present in wines, like polyphenols and polysaccharides.

Results show that CMC has a better inhibitory effect than polysaccharides at 10 times lower concentration and an equivalent inhibitory effect to that of polyphenols at 50 to 200 times lower concentration at 11,5 °C. Furthermore, the inhibitory effect is maintained at 2 °C, when the crystallisation risk is increased. In that case, 3 to 5 times greater concentration are needed to achieve the same effect than at 11.5 °C.

Refrigeration tests were performed on wines to record the presence or absence of crystals. Results from the experimental conditions (3 weeks at -4 °C for 20 white and red wines ; or 8 days at 30 °C followed by 2 months at 0 °C) show that 20 mg.L^{-1} CMC has an inhibitory effect on potassium hydrogen tartrate crystallization equivalent to 100 mg.L^{-1} metatartaric acid. Besides, the CMC efficiency increases in parallel with increasing CMC concentration, without showing any limiting efficiency.

The same observation is made for 10 wines heated for 8 days at 30 °C and then refrigerated for 2 months at 0 °C. This severe treatment reduces the metatartaric efficiency by 40 %. For 5 mg.L^{-1} CMC, 30 % of the wines have tartaric crystals and 20 % have other unidentified crystals. For 20 mg.L^{-1} CMC, 10 % of the wines have tartaric crystals and the same other 20 % have again unidentified crystalline haziness.

The efficiency of 20 mg.L^{-1} low molecular weight CMC that match the OIV-OENO 366-2009 and OIV-OENO 02/2008 resolution is confirmed to prevent tartaric acid salt precipitation, in agreement with other studies on the topic. With no impact on health, stable under heating and in acid solution, without viscosity effect at the very low concentration considered (Crachereau *et al.*, 2001), CMC is a new candidate for tartaric stabilization when its full dissolution before incorporation is achieved. However, the 20 mg.L^{-1} (2 g.hL^{-1}) dose should be reconsidered for practical application with the help of winemakers, depending on the local context of the wine supersaturation and storage

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