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Effect of an electric field on the heterogeneous nucleation and crystal growth of potassium hydrogen tartrate in wines

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Abstract

Potassium hydrogen tartrate (KHT) is a naturally occurring salt in wines. To avoid the formation of KHT crystals in bottles, it is necessary to stabilize wines before bottling. However, none of the current techniques is fully satisfactory. A new process, called the 'trap process', has been developed that consists of cold-crystallizing KHT on a stainless steel packing. To accelerate the heterogeneous nucleation and/or crystal growth rate of the salt, the influence of an external electric field on these phenomena was studied. A potentiostatic circuit maintained a constant potential against a saturated calomel electrode. A preliminary cyclic voltammetry study led to the determination of the most suitable potential values (i.e., inducing no electrochemical reaction). A set of wine stabilization experiments was then performed using the 'trap process' with and without potential. The results demonstrated that a potential of +200 mV vs SCE generates an increase in process efficiency, even in the case of wines containing a lot of inhibitors. It also significantly reduces the induction time of nucleation.

List of symbols

a	activity
C^*	KHT solubility in water per litre of solution (g L^{-1})
$(DO)_{275}$	optical density at 275 nm with respect to water
E	electric potential with respect to the saturated calomel electrode (mV)
E_0	initial potential against SCE (mV)
E_λ	reversal potential against SCE (mV)
HS	hydroalcoholic solution
H_2SO_4	sulfuric acid
i	current (mA)
[K]	potassium concentration (g L^{-1})
K_a	activity product
K_{ST}	thermodynamic solubility product
KHT	potassium hydrogen tartrate or potassium bitartrate
m_{rec}	KHT crystal mass recovered after stabilization per litre of solution (g L^{-1})
m_{seed}	KHT seed mass per litre of solution (g L^{-1})
R	red wine
Ro	rosé wine
S	supersaturation ratio
T	absolute temperature (K)
TA	total acidity (g H_2SO_4 L^{-1})
$[TH_2]$	total tartaric species concentration (g L^{-1})
t_{ind}	induction time (h)
T_{op}	operating temperature (°C)
TPI	total polyphenol index
V	alcoholic degree (vol %)
v	potential sweep rate (mV s^{-1})
W	white wine
wp	without potential

Greek symbols

κ	solution conductivity (mS cm^{-1})
$\Delta\kappa$	conductivity drop at constant temperature (mS cm^{-1})

1. Introduction

To avoid the risk of tartaric salt formation (especially potassium hydrogen tartrate) during wine conservation in bottles, wines have to be stabilized by adapted treatments before bottling. These techniques consist in eliminating a sufficient part of the potassium bitartrate in the form of crystals [1–5] or K^+ and TH^- ions [6–8], or in modifying the crystallization conditions by the addition of an inhibitor [9–14]. The first treatments are the most successful but they are expensive and can be inefficient. Therefore, a new stabilization process, called the 'trap process' [15–18], has been developed. In this technique, the potassium bitartrate crystallizes at low temperature (about −4 °C) preferentially on a stainless steel packing, previously seeded or not. To optimize the trap process, several parameters have been studied. As the trap is an electronic conductor, it should be possible to use it as an electrode to modulate the interfacial properties acting upon nucleation and crystal growth phenomena by variation of the local electric field at the trap/wine interface. The aim of this work is to investigate the influence of an external electric potential, applied to the metallic trap with respect to a reference electrode, on the KHT crystallization steps.

When an ionic salt crystallizes from a solution, ions move from one phase to another and this transfer induces an electric field. An electric potential difference is generally created between the two phases. According to Engell [19], the potential drop at the solution/substrate interface influences the rate of an electrochemical process and we can assume that this phenomenon applies to the crystallization of an ionic salt. The phase transformation rate would thus depend on the electric potential, in particular through the solid–liquid interfacial tension [20, 21] and the crystallization driving force [22, 23]. The relationship between the electric potential and the crystallization rate of a component can be studied in two ways: either the potential is imposed and the crystallization rate is determined, or the supersaturation ratio is imposed and the electric potential is measured. In the present work experiments were carried out with controlled potential.

Few experimental studies are described in the literature. Most work involves high values for the electric fields, which are not well suited to wine treatment, and do not allow the establishment of a predictive model for the effect of an electric potential on the crystallization rate of an ionic salt. For example, Hanani and Schieber [24] observed that an electric field (in the ranges 1–10 V cm^{-1} or 200–900 V cm^{-1}) decreases the growth rate of ferroelectric crystals of potassium sodium tartrate. Moreover, according to Marand et al. [25], an electric field greater than 0.5 MV cm^{-1} favours the formation of homogeneous nuclei of the polar phase of poly (vinylidene fluoride).

Our study is devoted to the modification of the KHT nucleation and/or crystal growth steps by application of a moderate electric potential to the metallic packing, where crystallization occurs. For this purpose, a preliminary experiment using cyclic voltammetry was realized in order to determine a range of suitable potentials to apply to the trap which induced neither the occurrence of electrochemical reaction nor pH variation, which would be detrimental to the wines. A set of wine stabilization runs was then carried out both with and without electric field to estimate the effect of this parameter on the KHT crystallization. A synthetic hydroalcoholic solution was used as a reference compound allowing a better comprehension of the results obtained with actual wines and hence of the influence of the operating parameters.

2. Materials

The wines used in our experiments came from different French regions. The synthetic hydroalcoholic solution was prepared mixing an 11% ethanol–water solution with 2.42 g L^{-1} of KHT and 2 g L^{-1} of potassium sulfate. K_2SO_4 provides the potassium ions in excess with respect to the bitartrate ions present in wines. The main characteristics of the wines used and of the hydroalcoholic solution are listed in Table 1.

The supersaturation ratio is defined as follows:

Table 1. Characteristics of the wines and of the hydroalcoholic solution

Solutions	pH	V /vol %	TA /g H_2SO_4 L^{-1}	$[TH_2]$ /g L^{-1}	[K] /g L^{-1}	TPI	T_{op} /°C	$S_{T_{op}}$
W1	2.9	11.5	5.24	2.9	0.34	6	−4	1.53
W2	3.1	11.5	4.56	1.96	0.46	8	−4	1.64
W3	3.8	13.1	4.8	0.96	1.71	11	−4	2.26
Ro	3.4	12.4	3.46	1.5	0.57	10	−4	1.47
R1	3.6	10.8	3.71	1.55	1.02	27	−4	1.61
R2	3.7	10.7	3.33	1.93	1.17	29	−4	2.74
R3	3.4	11.9	3.6	1.42	0.59	28	−4	2.28
R4	3.6	11.7	3.76	1.31	0.81	32	−4	2.12
R5	3.7	11.1	3.55	1.7	0.94	45	−4	2.4
R6	3.7	11.8	3.36	2.04	0.92	43	−4	2.62
R7	3.7	11.1	3.46	2.02	1.03	34	−4	2.69
R8	3.5	12.7	3.01	2.37	0.98	41	−4	1.75
HS	3.6	11	0.47	1.93	1.2	0	15	1.36

$$S_T = \sqrt{\frac{K_a(T)}{K_{ST}(T)}} = \sqrt{\frac{a_{K^+} \times a_{TH^-}}{K_{ST}(T)}} \quad (1)$$

where K_{ST} depends only on the temperature and on the solvent nature. K_{ST} is equal to the thermodynamic solubility product of KHT in the corresponding hydro-alcoholic solution (same alcoholic degree as the wine) and is expressed as follows [10]:

$$K_{ST}(T) = a_0 + a_1 V + a_2 V^2 \quad (2)$$

where:

$$\log(a_0) = -44.5368 + 2.5611 \times 10^{-1}\, T - 3.962 \times 10^{-4} T^2 \quad (3)$$

$$\log(-a_1) = -41.3051 + 2.2715 \times 10^{-1}\, T - 3.469 \times 10^{-4} T^2 \quad (4)$$

$$\log(a_2) = -16.078 + 3.998 \times 10^{-2}\, T - 1.925 \times 10^{-5} T^2 \quad (5)$$

The polyphenolic compounds are present in the colloidal phase [26]. They are inhibitors of KHT crystallization as they are adsorbed on the growth sites of the crystalline faces [27], thus blocking the crystal growth process. Measurements of the optical density at 275 nm (DO_{275}) of a diluted wine sample led to the determination of the total polyphenolic compounds quantity:

$$TPI = DO_{275} \times \text{dilution} \quad (6)$$

Wine is watered down 50 or 100 times to limit as much as possible the absorption due to any other wine components (alcohols, acids, SO_2). The total polyphenol indices measured for the studied wines, representative of a wide variety of wines, show that polyphenolic compounds are present in greater quantity in red wines than in white ones.

3. Apparatus and procedure

3.1. *Experimental device*

The apparatus used for the crystallization runs with or without electric field is shown in Figure 1. It consisted of four parts:

(i) A 6 L double jacketed and mechanically stirred reactor provided with a baffled draft-tube. Two sets of stainless steel packing were rolled up around the tube in inverse order so as to fill the space between the vessel and the draft-tube. This arrangement led to better circulation of the solution inside the trap (Figure 2).

(ii) A recording system for the solution temperature and conductivity.

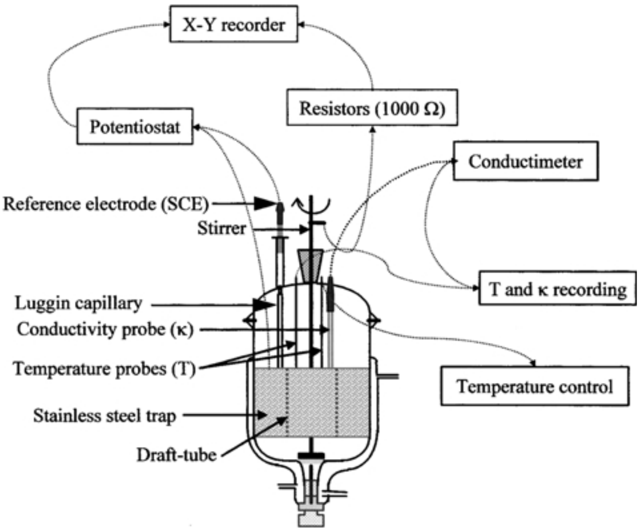

Fig. 1. Experimental apparatus.

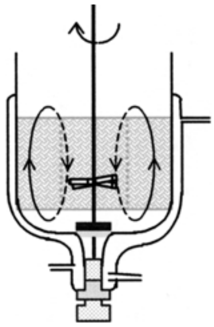

Fig. 2. Circulation of the solution inside the trap.

(iii) A control system for the solution temperature (HAAKE cryostat).

(iv) An electrochemical system allowing the application of a constant electric potential to the trap with respect to a reference electrode. A stainless steel wire constituted the working electrode (WE). The metal impeller was used as the auxiliary electrode (AE). The reference electrode was a saturated calomel electrode (SCE) in contact with the solution via a Luggin capillary, filled with the same solution. The electrodes were connected to a potentiostat, with a triangular signal generator. The amplitude and the slope of the generated signal were adjustable. The variations of current intensity during stabilization were plotted on an X–Y recorder.

Preliminary runs using cyclic voltammetry were carried out with similar equipment, but in a 150 mL reactor. For these experiments, the working and auxiliary electrodes consisted of a part of the metallic packing.

3.2. *Procedure*

3.2.1. *Trap seeding*

Trap seeding allowed the deposition of KHT crystals on the packing from an aqueous solution of potassium hydrogen tartrate. To prepare this solution, two temperatures, T_1 and T_2, were chosen according to the mass of seed to be deposited on the trap:

$$m_{\text{seed}} = C^*_{T_1} - C^*_{T_2} \tag{7}$$

where the KHT solubility in water was expressed by the following empirical law [17, 28, 29]:

$$C^*_T = -5940.18 + 77.58 \times T - 0.801 \times T^2 + 8.07 \times 10^{-4} \times T^3 - 6.32 \times 10^{-7} \times T^4 \tag{8}$$

The KHT crystal quantity $C^*_{T_1}$ was dissolved in pure water 15 °C over the selected temperature T_1 for about 2 h. The solution was then cooled as quickly as possible to a temperature T_2', slightly greater than T_2. At this temperature, the trap was introduced into the vessel to avoid KHT crystallization without the trap. The solution temperature was then reduced to T_2. The seeding was stopped when the conductivity drop corresponding to the crystallization of the desired seed mass was reached. An empirical relation between $\Delta\kappa_{\text{seed}}$ and m_{seed} was established from results of several trap seedings [17]:

$$\Delta\kappa_{\text{seed}} = \frac{m_{\text{seed}}}{2.10 \pm 0.29} \tag{9}$$

At the end of the seeding, the trap was removed from the reactor and dried at 50 °C for 4–5 h. The deposited KHT mass was determined by weighing.

Trap seeding reduces the induction time to zero. This parameter represents the period of time for the first crystal appearance. This phenomenon is detected by a drop in solution conductivity due to a decrease in amount of the K^+ and TH^- ions in the bulk solution (Figure 3). When the trap is seeded beforehand, KHT elimination from the wine occurs mainly by crystal growth of the seeds already deposited on the packing. The time needed for wine stabilization is thus reduced.

3.2.2. *Cyclic voltammetry*

The solution (wine or hydroalcoholic solution) was poured into the vessel and cooled to the desired temperature. A linear potential sweep was imposed on the trap and the current between the working and the auxiliary electrodes was recorded. Three parameters were studied: potential sweep rate ($5\ \text{mV s}^{-1} < v < 100\ \text{mV s}^{-1}$), solution temperature ($-4\ °\text{C} < T < 25\ °\text{C}$) and E_0 and E_λ values. For each set of parameter values, several potential sweeps were recorded.

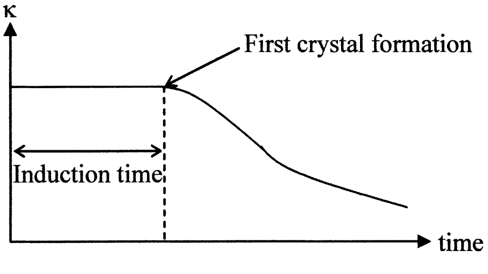

Fig. 3. Determination of the induction time.

3.2.3. *Stabilization runs with and without electric field*

Stabilization runs were carried out using the trap process. The solution (wine or hydroalcoholic solution) was poured into the reactor and cooled as quickly as possible to the desired operating temperature. This temperature was held constant during the run. The stirring speed was fixed at 520 rpm. The stainless steel trap, seeded beforehand or not, was then introduced into the vessel and removed after 2.5 h, the time interval corresponding to the wine stabilization. For some experiments, a constant potential was also applied to the packing. The solution conductivity was computer recorded every 3 s. After each treatment, the trap was dried at 50 °C for 4–5 h and the KHT mass crystallized during the run was evaluated by weighing.

4. Results and discussion

4.1. *Choice of potential range*

In the range of temperature [−4 °C; 25 °C] and for potential sweep rates between 5 mV s^{-1} and 100 mV s^{-1}, the typical shape of the current–voltage curves is shown in Figures 4 and 5. The influence of E_0 and E_λ values is not presented here since no additional information was yielded.

The voltammograms of the wines and the hydroalcoholic solution have similar shapes. The voltammograms show the reduction and the oxidation of the solvent on the stainless steel and the reduction of dissolved oxygen ($E_{\text{SCE}} \cong -0.15$ V).

In the range of potential values (0 mV to +400 mV), no characteristic peak due to an electrochemical reaction was observed. For a given temperature, the current obtained is low ($-2\ \text{mA} < i < 3.5\ \text{mA}$) (Figure 4) and assumed to be capacitive. In fact, for a given potential value, the current measured between the working and counter electrodes is proportional to the potential sweep rate. Thus, there is probably no electrochemical reaction

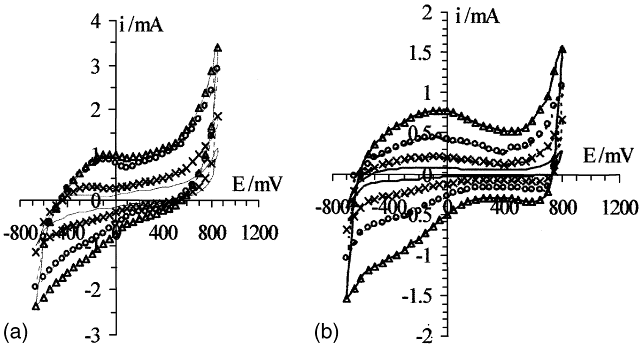

Fig. 4. Influence of potential sweep on cyclic voltammograms at $T = 25$ °C. (a) Red wine, R2 and (b) hydroalcoholic solution, HS. Sweep, *v*: (——) 5, (×) 20, (○) 50 and (△) 100 mV s^{-1}.

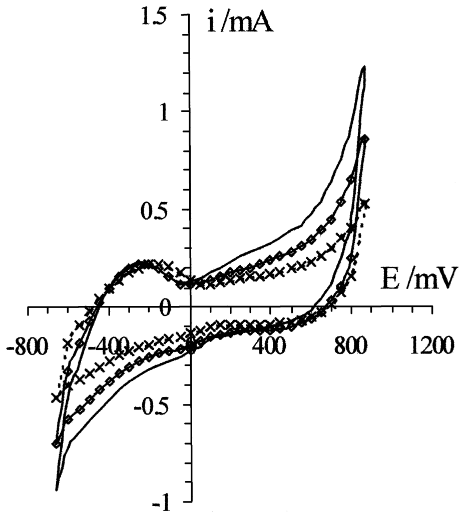

Fig. 5. Influence of temperature on the cyclic voltammogram obtained from the red wine R2 at a scan rate of 10 mV s^{-1}. Temperature, *T*: (——) 20, (◇) 10 and (×) −4 °C.

in this range. However, for a given sweep rate, the range of suitable potentials is larger as the temperature decreases (Figure 5).

Our results indicate that the potential applied to the trap during the crystallization runs has to be within the range (0 mV to +400 mV).

4.2. *Potential effect on the KHT heterogeneous nucleation*

During the nucleation process, new particles called nuclei are formed in the system. When the solution contains no crystals of the species to be crystallized, the nucleation is called primary nucleation. Moreover, if the nuclei are formed on a solid substrate, the process is called primary heterogeneous nucleation. In order to study the effect of an external electric field on the KHT heterogeneous nucleation, some stabilization runs of the red wine R2 and the hydroalcoholic solution HS were carried out with the unseeded trap, with and without an applied potential of +200 mV vs SCE (Table 2). As the solutions are KHT crystal-free, we can assume that there is only heterogeneous nucleation, i.e. that there is only formation of new particles, at the beginning of the experiment (during 1.5 h). After this lapse of time, the crystal growth can no longer be neglected. The slope change in the variation of the recovered KHT mass against time (Figure 6) gives evidence of this phenomenon.

Analysis of the results shows that a +200 mV potential applied to the packing tends to decrease the induction time of the potassium bitartrate. It then promotes the heterogeneous nucleation process, in particular for red wine R2. Furthermore, for the hydroalcoholic solution, the amount of KHT recovered is more significant in the presence of the electric field. The results indicate that a +200 mV potential favours the KHT heterogeneous nucleation on the trap. Thus, the seeding step could perhaps be suppressed for stabilization in the presence of an electric field.

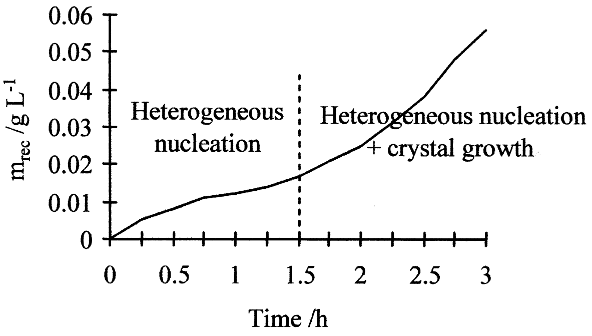

Fig. 6. Crystallization process against time for the solution HS.

4.3. *Potential effect on the KHT crystallization*

Wine stabilizations were carried out at −4 °C for 2.5 h. For some runs, a constant potential of +200 mV vs SCE was applied to the metallic packing. The quantities of

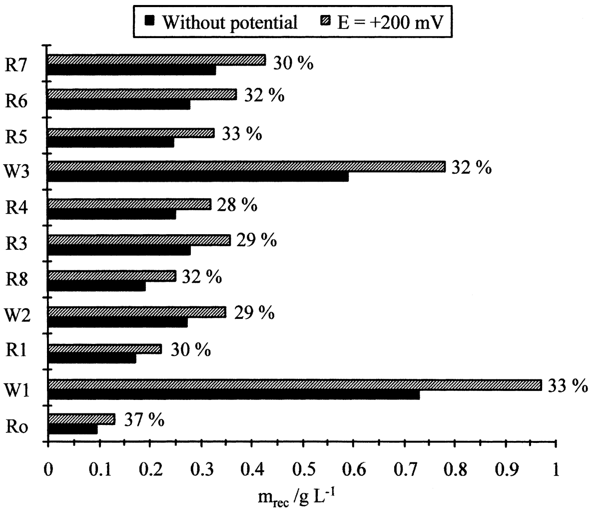

Fig. 7. Effect of a +200 mV potential on the 2.5 h stabilization efficiency.

Table 2. Influence of electric potential on the KHT heterogeneous nucleation

Solutions	t_{ind}/h		m_{rec}/g L^{-1}	
	Without potential	E_{SCE} = +0.2 V	Without potential	E_{SCE} = +0.2 V
R2	≫48	15	/	/
HS	3	0	0.02	0.56

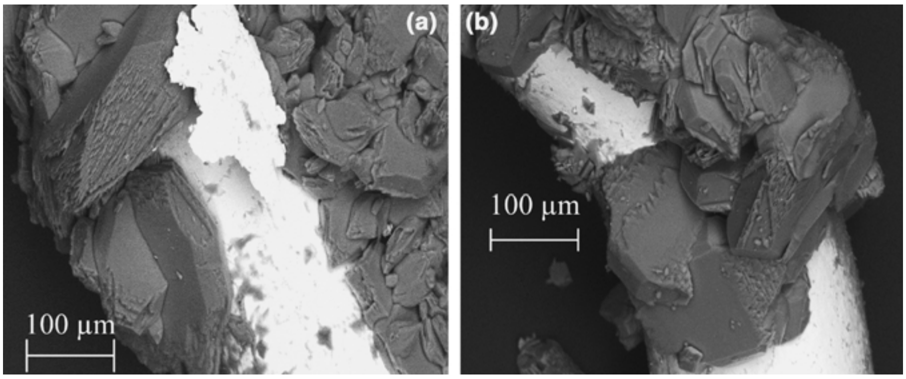

Fig. 8. Morphology of KHT crystals formed from red wine R3. (a) Without potential; (b) with $E = +0.2$ v.

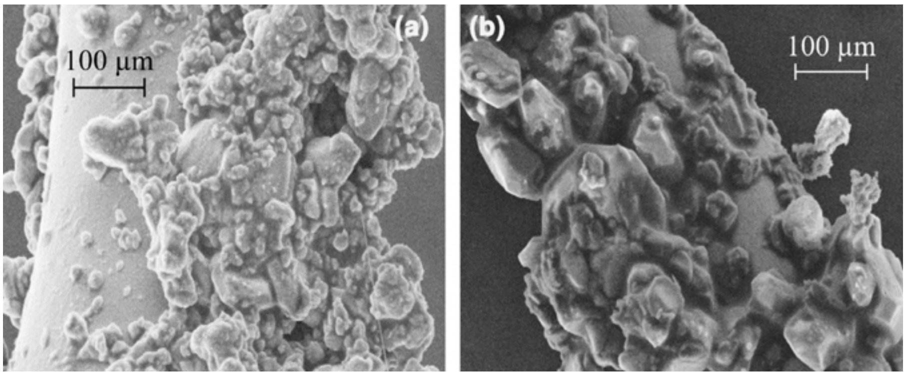

Fig. 9. Morphology of KHT crystals formed from white wine W3. (a) Without potential; (b) with $E = +0.2$ V.

KHT recovered are plotted in Figure 7. The percentage relative mass gain, G_{rm}, defined as follows, is also shown in the Figure:

$$G_{\mathrm{rm}} = \frac{m_{\mathrm{rec}}^{200\ \mathrm{mV}} - m_{\mathrm{rec}}^{\mathrm{wp}}}{m_{\mathrm{rec}}^{\mathrm{wp}}} \times 100 \tag{10}$$

Comparison of the values reported in Table 1 and in Figure 8 shows that for a similar TPI the KHT mass recovered, with or without potential, is an increasing function of the supersaturation ratio (wines Ro, W2 and W3; R5, R6 and R8). In the same way, for a similar initial supersaturation, the KHT quantity recovered with or without potential increases when the total polyphenol index decreases (wines W1, R1 and W2; R5, R6 and R7).

Furthermore, for all treated wines, the KHT mass recovered per litre of wine is greater when a constant potential is imposed. The relative enhancement of mass is equal to 31 ± 2% by applying 200 mV vs SCE. This increase is independent of the initial supersaturation and TPI.

Finally, the crystals deposited on the stainless steel wires during stabilization with and without potential were observed by SEM. Figures 8 and 9 represent the photographs obtained with the wines R3 and W3. The crystal morphology produced by the trap process seems to be unaffected by the potential conduction.

5. Conclusions

The influence of an external electric field on the crystallization of potassium hydrogen tartrate on a metallic packing was studied. A preliminary study by cyclic voltammetry led to the determination of a suitable potential range (0 mV to +400 mV).

All runs carried out with the unseeded trap showed that a +200 mV potential allows a reduction of the induction time and an increase in the heterogeneous nucleation rate.

In any case, stabilization runs achieved with the seeded trap proved the positive effect of the electric field for all treated wines (rosé, white and red). Application of +200 mV vs SCE to the packing allowed relative enhancement of recovered KHT by approximately 31%.

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