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A study of calcium salt precipitation in solutions of malic and tartaric acid

by

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Die Ausfällung von Calciumsalzen aus Lösungen von Wein- und Äpfelsäure

Zusammenfassung: Die Ausfällung von Calciumsalzen wurde an Lösungen von L(+)-Weinsäure und L(-)-Äpfelsäure in Wasser oder einem Ethanol-Wasser-Gemisch untersucht. Calciumtartrat und Calciummalat wurden zwar unabhängig voneinander ausgefällt, beeinflussten sich aber gegenseitig. Die Auskristallisierung von Calciummalat war stark abhängig von Impfkristallen. Calciummalat und Calciumtartrat können als Impfpartikel für die Calciummalat-Ausfällung fungieren. Es konnte kein Beleg für die Ausfällung eines Malat-Tartrat-Doppelsalzes gefunden werden.

Die Kinetik der Kristallisation zeigte, daß der Großteil des Calciumtartrates sehr rasch während eines frühen Prozesses dritter Ordnung ausgefällt wurde, dem später ein weiterer Prozeß dritter Ordnung folgte. Die Ausfällung von Calciummalat vollzog sich langsam in zwei Phasen (ähnlich wie beim Calciumtartrat), wobei jedoch die zweite Phase viele Tage andauerte. Durch die Beigabe von Impfkristallen veränderte sich die Ausfällung von Calciummalat zu einem Prozeß erster Ordnung. Die Bildungskonstanten wurden für die verschiedenen Phasen bestimmt.

Calciumcarbonat führte zu einer schnelleren Auskristallisierung von Calciummalat und -tartrat als Calciumhydroxid. Ethanol erhöhte generell die Kristallisationsrate von Calciumtartrat, während dies für Calciummalat nur in Verbindung mit Calciumcarbonat zutraf.

Key words: tartaric acid, malic acid, calcium, carbonate, solution, deposit, crystallisation, kinetics, seed crystal.

Introduction

Chemical deacidification, specifically partial neutralization and removal of organic acids from the must or wine, is a desirable alternative to the more extensive malolactic fermentation. This procedure is able to lower both malic and tartaric acid concentrations in either must or wine.

The double salt treatment does not always work as might be expected. Although it has been reported to be effective in some cases, at other times it removes only tartaric acid or may produce little reduction in malate concentration (NAGEL 1977; MATTICK *et al.* 1980).

The aim of this study was to investigate the extent and kinetics of the reactions involved in the neutralization of malic and tartaric acids by calcium carbonate.

Literature review

The double salt

The formation of a calcium malate-tartrate double salt in wine residues was first reported by ORDONNEAU (1891). Using calcium carbonate and hydroxide, he noted that two types of crystals had formed and the needle-shaped crystals contained calcium,

tartrate and malate which he described as a double salt. An alternative explanation would be a layered mixture of two different salts. Such crystals would not be distinguished from a double salt by compositional analysis.

The double salt procedure

The current double salt deacidification procedure is based upon the work of MUNZ (1960). His experiments, which used model solutions, displayed a rapid precipitation of calcium tartrate within 15 min. This was followed by the much slower formation of hedgehog-shaped crystals thought to be the calcium malate-tartrate double salt, over the following 3–4 h. Unfortunately, only initial and final concentrations of the treatment were noted.

Modified double salt procedure

KIEHLHÖFER and WÜRDIG (1963) proposed an improvement in the procedure by adding a portion of the fraction of must to be treated to the calcium carbonate to increase the pH to 5.0 initially. The remainder was then added to lower the pH to 4.5 and to complete the treatment. This modification was said to enhance the formation of the double salt.

WÜRDIG (1976) described the double salt precipitation as often occurring along with the precipitation of calcium tartrate. He claimed that pure double salt precipitation was only obtained when malic acid was in excess of tartaric acid by 50–80%. STEELE and KUNKEE (1978, 1979) stated that in order to remove equimolar amounts of malic and tartaric acid it is necessary to have a pH in the treated fraction of at least 4.5 in must (5.1 in wine) and a malic acid content equal to or greater than the tartaric acid content.

WÜRDIG (1976, 1977) described the neutralization of malic acid by the addition of potassium and calcium carbonates. He found that the malate solutions which formed were unlike those of the tartrate in that they had an unpleasant salty and paper-like flavor. Taste threshold levels and the residual potassium or calcium malate concentrations in the wine were not presented.

WÜRDIG *et al.* (1983) further modified the deacidification procedure by the addition of calcium tartrate some 2 h later. This modification enhanced the precipitation of the double salt after 96 h in one wine. Reductions of 21.2 mmol/l in tartaric acid and 56.2 mmol/l in malic acid, or over 2.5 times that of the tartrate, were noted. Calcium malate not in a double salt must have been precipitating from the wine to produce these results.

STEELE and KUNKEE (1978, 1979) observed a greater molar decrease in tartaric than malic acid in both musts and wines, which they attributed to less malic than tartaric acid. They concluded that the tartrate loss was a combination of calcium double salt, potassium bitartrate precipitation, and the long-term precipitation of calcium tartrate. The malic acid loss was attributed to double salt formation and yeast utilization of some malic acid during fermentation. Calcium malate precipitation was not considered as a factor in the malate concentration decline.

Temperature effects

WÜRDIG *et al.* (1983) studied the effect of temperature on the treatment. They found more malate and tartrate removal, after 65 h, with decreasing temperature of 25, 20, and 15°C.

Solubility product estimates

A solubility product of the calcium malate-tartrate double salt was proposed by

WÜRDIG (1976) and calculated to be:

$$[\text{Tartrate}^{--}] \times [\text{Malate}^{--}] \times [\text{Calcium}^{++}]^2 = 2.1 \times 10^{-10}$$

Later, WÜRDIG (1985) reported the product in a succinate buffer, with 10 % ethanol, to be 5.4×10^{-11} . It is not clear whether the ion activities were included in these calculations.

Calcium malate is much more soluble in water than calcium tartrate, but much less soluble in 95 % alcohol (LINKE 1958; STEPHEN and STEPHEN 1963). This would suggest that wine treatments would be more effective for calcium malate precipitation.

Materials and methods

The solutions

Two different solutions were used in these experiments, either a solution 40 mM in both tartaric acid and malic acid or a 40 mM malic acid solution (L(-)malic acid, L(+)-tartaric acid, L(+)-calcium tartrate, and calcium hydroxide reagents from Sigma Chemical (St. Louis, MO, USA); calcium carbonate reagent from Mallinckrodt (St. Louis, MO, USA)). All solutions were made with double distilled water.

During the crystallization, samples were taken from the solution at various times. They were removed with a syringe and immediately filtered through a 0.8 μm membrane filter. Concentrated nitric acid was added to redissolve any later precipitation.

Tartrate and malate determinations

Malic and tartaric acids were determined by high performance liquid chromatography. The system consisted of a Bio-Rad Laboratories (Richmond, CA, USA) model 1330 pump, a Waters Associates (Milford, MA, USA) differential refractometer, model R401, a Bio-Rad Aminex ion exclusion column, model HPX-87H (300 \times 7.8 mm), heated to 65 $^{\circ}\text{C}$, and a Shimadzu (Kyoto, Japan) model C-R3A Chromatopac integrator. The mobile phase was 0.05 N sulfuric acid in double distilled water, membrane filtered (0.8 μm) and degassed.

Calcium determination

Calcium concentration was determined by atomic absorption spectroscopy, using a Perkin-Elmer (Norwalk, CT, USA) atomic absorption spectrophotometer, model 2380, with an air-acetylene fuel system.

Samples were diluted to the desired range with a Hamilton digital diluter, model 100004 (Reno, NV, USA). Lanthanum oxide was added to a final concentration of 1000 mg/l to prevent chemical interference in the calcium determination.

Seed crystal preparation

Seed crystals were prepared using a Büchi (Flawil, Switzerland) Rotavapor-R vacuum evaporation system, with a refrigerated condenser and 30 $^{\circ}\text{C}$ water bath.

Seed crystals were sieved to the desired size range (355 — 425 μm) with ASTM screens (W. S. Tyler, Menton, OH, USA).

Interpretation of kinetic data

The data were analysed to determine the order of the rate of reaction. A computer program (COLE 1986) plotted transforms of concentration versus time to determine the

order of the reactions. The program performed a linear regression and calculated the rate constant from the slope and its standard deviation. The correlation coefficient and the F-ratio for the slope were also calculated.

Results and discussion

The crystallization of the calcium salts from solution was followed for several conditions. A summary of the different experiments is presented in Table 1.

The first two experiments were duplicates of the work done by MÜNZ (1960), though at twice the concentrations he used to more closely simulate the acid levels found in high acid musts and wines. The plots of acid concentration versus time for Experiments 1 and 2 are shown in Fig. 1. In both experiments there is a sharp initial decline in tartarate concentration, from 40 mmol/l to less than 4 mmol/l within the first 10 min. This is due to the rapid initial precipitation of calcium tartarate from solution. During this period the malate concentration in solution underwent little change. After 10 min, the solution contained 75–95% of the initial malate and less than 10% of the initial tartarate concentration.

If precipitation of a calcium malate-tartrate double salt had occurred, there would have been a parallel decline in the malate and tartrate concentration curves. One region of parallel decline is found in the initial precipitation period. The malate depletion curve goes through a rapid initial decline, much shorter than that for tartrate, and then a relatively long period of slow decrease. The relative independence of these two curves indicates that the initial decline in malate and tartrate is due to the precipitation of calcium malate and calcium tartarate. The rates of reactions will be discussed

Table 1

Summary of experiments

Übersicht über das Versuchsprogramm

Expt. no.	Malic acid (M)	Tartaric acid (M)	Calcium source and concentr. (M)	Solution	Seed crystals
1	0.04	0.04	CaCO ₃ 0.08	Water	None
2	0.04	0.04	CaCO ₃ 0.08	ETOH/water	None
3	0.04	0.04	Ca(OH) ₂ 0.08	Water	None
4	0.04	0.04	Ca(OH) ₂ 0.08	ETOH/water	None
5	0.04	0.04	CaCO ₃ 0.08	ETOH/water	CaMa 5 g/l
6	0.04	—	CaCO ₃ 0.04	Water	None
7	0.04	—	CaCO ₃ 0.04	ETOH/water	None
8	0.04	—	CaCO ₃ 0.08	Water	None
9	0.04	—	CaCO ₃ 0.08	ETOH/water	None
10	0.04	—	CaCO ₃ 0.08	ETOH/water	CaMa 5 g/l

later. After approximately 20 min and for several h, the calcium and malate concentrations change little. MÜNZ concluded that double salt precipitation occurred during this time.

The malate concentration in each solution continues to decline for 5–8 d (Table 2). This indicates that, although the driving force for precipitation exists, the rate of calcium malate crystallization is very slow.

An alternative view is given by the change in calcium concentration with time (Fig. 2). The calcium content appears to go through four distinct phases. First, there is a rapid initial increase in calcium concentration as calcium carbonate dissolves in solution until it reaches saturation. The solubility is limited by the evolution of carbon dioxide from solution at this pH.

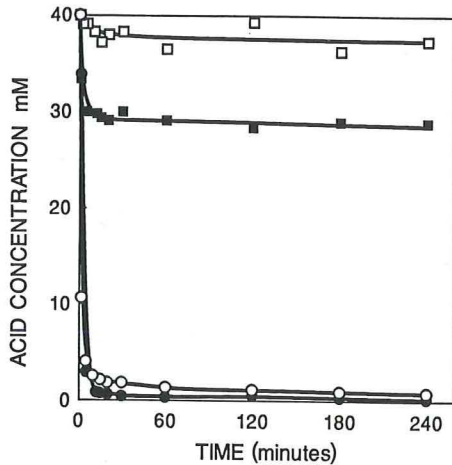


Fig. 1: Disappearance of tartrate (○, ●) and malate (□, ■) with time, Experiments 1 (○, □) and 2 (●, ■) from Table 1.

Abnahme von Tartrat (○, ●) und Malat (□, ■). Versuch 1 (○, □) und 2 (●, ■) von Tabelle 1.

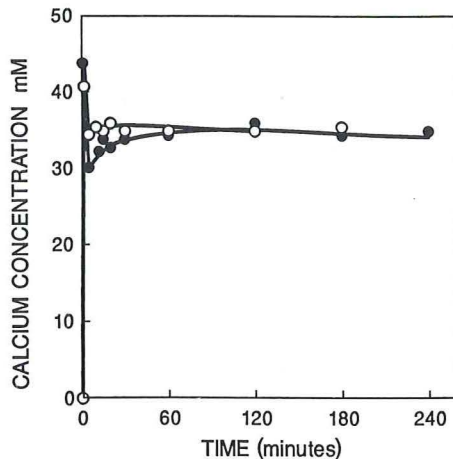


Fig. 2: Calcium concentration versus time, Experiments 1 (○) and 2 (●) from Table 1.

Veränderung der Calciumkonzentration. Versuche 1 (○) und 2 (●) von Tabelle 1.

The next phase is a sharp decline which is due to the rapid precipitation of calcium tartrate. This parallels the decrease in tartrate concentration in solution (Fig. 1). During this period, the rate of precipitation (CaTa) exceeds the rate of dissolution (CaCO₃) and the calcium concentration decreases. This decline is limited by the amount of tartrate in solution which falls to below 4 mmol/l at 5 min, in both the water and ethanol/water solutions (Fig. 1).

The third phase is when more calcium is entering than leaving the solution. The remaining phase is then the slow precipitation of calcium malate in Fig. 1 and Table 2.

Table 2

Malate, tartrate, and calcium concentrations 3 h, 4 h and several d after beginning of the experiments
Malat-, Tartrat- und Calciumkonzentration 3 h, 4 h und einige d nach Versuchsbeginn

Expt. no.	Concentration (M)		
	3 h	4 h	Long term
1 Ma	0.0363	0.0374	0.0131
Ca	0.0354	0.0418	0.0185
Ta	0.0010	0.0009	0.0007
2 Ma	0.0290	0.0289	0.0102
Ca	0.0343	0.0348	0.0140
Ta	0.0004	0.0003	0.0002
3 Ma	0.0234	0.0221	0.0093
Ca	0.0342	0.0294	0.0154
Ta	0.0011	0.0012	0.0010
4 Ma	0.0353	0.0322	0.0301
Ca	0.0379	0.0369	0.0333
Ta	0	0	0
5 Ma	0.0227	—	0.0215
Ca	0.0265	—	0.0238
Ta	0.0004	—	0
6 Ma	0.0394	—	—
Ca	0.0401	—	—
7 Ma	0.0406	—	0.0397
Ca	0.0414	—	0.0457
8 Ma	0.0393	—	0.0406
Ca	0.0389	—	0.0400
9 Ma	0.0402	—	0.0335
Ca	0.0383	—	0.0406
10 Ma	0.0271	0.0302	—
Ca	0.0279	0.0331	—

Effects of ethanol on calcium salt precipitation

The effect of ethanol was to decrease the solubility of calcium salts in solution. In Fig. 1, the concentration of both malate and tartrate in solution at a given time is much lower in the ethanol/water solution than in the water alone.

The ethanol also increases the rate of precipitation due to increased supersaturation. This is seen in the rate of decrease in the acid concentrations (Fig. 1). The rate of removal of malate from water is much slower than that from the ethanol solution. The same is true for tartrate, although this is only apparent at lower concentration since the initial rate of decrease is very fast.

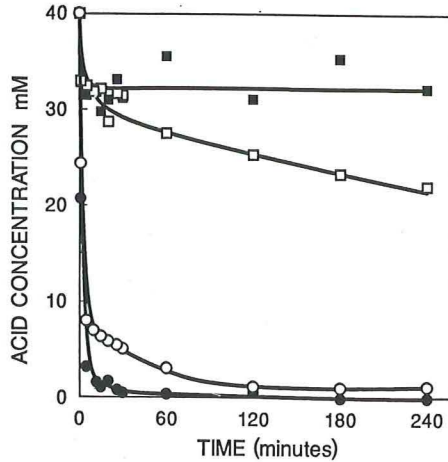


Fig. 3: Disappearance of tartrate (○, ●) and malate (□, ■) with time, Experiments 3 (○, □) and 4 (●, ■) from Table 1.

Abnahme von Tartrat (○, ●) und Malat (□, ■). Versuche 3 (○, □) und 4 (●, ■) von Tabelle 1.

Effect of different calcium sources

Experiments 3 and 4 examined the effect of using calcium hydroxide instead of calcium carbonate. It is a more soluble calcium source and is not involved in the carbon dioxide-carbonate equilibrium. The greater solubility is demonstrated by the higher calcium concentration in Experiments 3 and 4 than in 1 and 2 (Figs. 2 and 4).

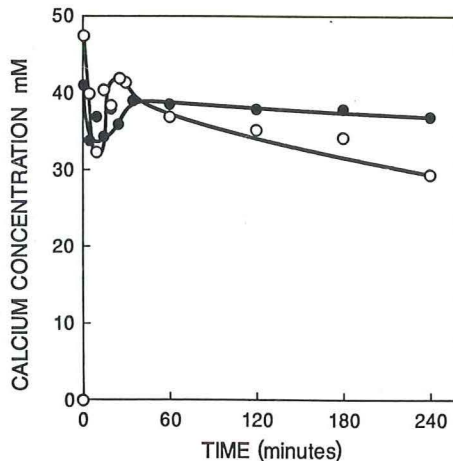


Fig. 4: Calcium concentration versus time, Experiments 3 (○) and 4 (●) from Table 1.

Veränderung der Calciumkonzentration. Versuche 3 (○) und 4 (●) von Tabelle 1.

The pH is much higher with calcium hydroxide (pH 11—12) than with calcium carbonate (pH 4—7). This ensures that all of the malic acid is in the malate ion form. The net effect of this is to increase the concentration product of calcium malate. As mentioned previously, ethanol enhanced the overall rate of precipitation of both salts in the calcium carbonate treatment, as well as the tartrate in the calcium hydroxide treatment. The rate of precipitation of malate is much less for the ethanol/water solution than in water alone (Fig. 3). This occurs even though the solubility of calcium malate is much lower. This slowing of the rate by ethanol was not apparent in the calcium malate precipitation of the calcium carbonate treatment, possibly because of the more significant effect of the calcium carbonate seed particles. The decrease in tartrate concentration in the ethanol/water solution is nearly identical to that of tartrate in water (Fig. 3 versus Fig. 1). There is a slower and more gradual decline in the hydroxide case than the carbonate case. Again, this may be due to the effect of nuclei (of calcium carbonate) increasing the rate of calcium tartrate precipitation. The calcium concentration in Experiments 4 and 5 (Fig. 4) appears to go through the same four phases of precipitation noted earlier.

Calcium malate precipitation

To remove the influence of calcium tartrate on the precipitation of calcium malate, Experiments 6, 7, 8, and 9 were done with only calcium malate precipitating from solution. In Experiments 6, 7, and 8, there was no precipitation of calcium malate even after 1 week. Only in Experiment 9, there was any decrease in malate concentration at all and then only in the very long term. This contrasts with the rapid depletion of at least some malate in each of the malate/tartrate solutions. This behaviour suggests that in the malate/tartrate solutions there is some effect of the calcium tartrate which enhances calcium malate precipitation. One explanation of this phenomenon is that the calcium tartrate crystals act as promoters, either as specific nuclei for growth or as particles which aid in the generation of calcium malate nuclei and their precipitation. This nucleus effect would result in crystals with a calcium tartrate core, surrounded by a calcium malate coating and this may explain why some studies have reported crystals that contained both tartrate and malate. The alternative, nucleation by turbulence promotion, would yield two distinct crystal types, the malate and the tartrate.

Effect of seed crystals

This effect was tested in Experiment 10, where calcium malate precipitation was followed with added seed crystals. The conditions were identical to Experiment 9, except 5 g/l calcium malate seed crystals were added to the solution with the calcium carbonate. The malate concentration continually declined throughout the experiment and was very similar to the malate curve of Experiment 1 (ethanol/water solution) in Fig. 2. The calcium concentration followed much the same pattern as the earlier calcium plots, though the calcium concentration decreased more quickly after 10 min than in Experiments 1 and 2. These results are particularly interesting in light of Experiments 6—9 in which little to no precipitation occurred in any of the combinations. This experiment shows that calcium malate can be precipitated, but the limiting factor is the number of nucleating sites upon which crystal growth may occur.

In Experiment 5, a solution identical to that of Experiment 2 was prepared and 5 g/l calcium malate seed crystals were added with the calcium carbonate. As shown in Fig. 5, the calcium malate concentration decrease is initially slower with the added seed crystals, indicating a less dramatic nucleation phase than in the malate/tartrate solution without the added seed crystals. The second crystallization phase appears to be much more rapid, with a steeper decrease in malate concentration between 20 and 180 min with the added seed crystals. This is confirmed by the parallel decrease in calcium concentration between 20 and 180 min in Fig. 6.

The tartrate concentration drops quickly and virtually identically in the first 5 min in both Experiments 5 and 2, indicating that the same rapid initial precipitation of calcium tartrate occurs in both systems.

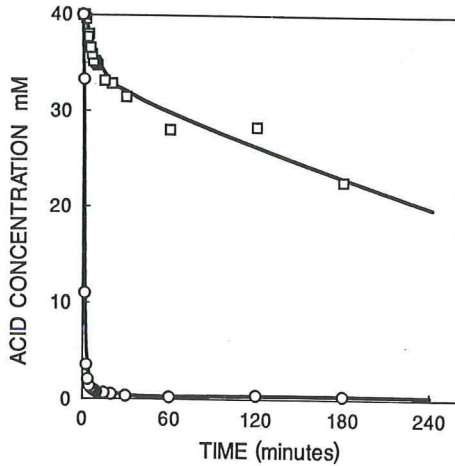


Fig. 5: Disappearance of tartrate (○) and malate (□) with time, Experiment 5 from Table 1.

Abnahme von Tartrat (○) und Malat (□). Versuch 5 von Tabelle 1.

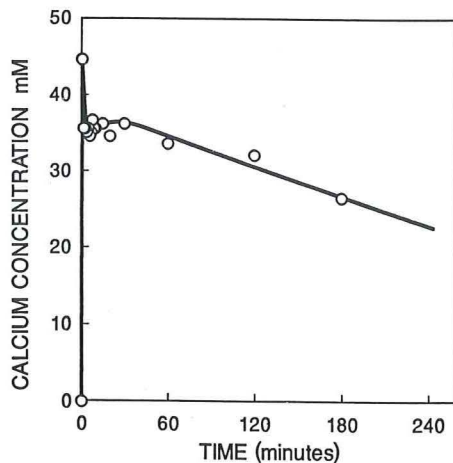


Fig. 6: Calcium concentration versus time, Experiment 5 from Table 1.

Veränderung der Calciumkonzentration. Versuch 5 von Tabelle 1.

Solubility product estimates

The solubility products of calcium malate, calcium tartrate and the 'double salt' were estimated from the final equilibrium concentrations given in Table 2. These are compared with other published values (Table 3). The reported solubility products do not usually specify either the buffer concentration or whether ion activity was considered. It is not known whether these solutions actually reached equilibrium, as precipitation continued for at least 50 d in some of our experiments. All the calculated solubility products are relatively close in value and are within an order of magnitude of those reported in the literature, except for that of the first value of WURDIG (1976).

Table 3

Solubility product summary
Zusammenfassung der Löslichkeitsprodukte

Expt. no. and literature data	Calcium malate ($\times 10^{-9}$)	Calcium tartrate ($\times 10^{-9}$)	Double salt ($\times 10^{-11}$)
1 — 8 d	3.60	1.92	6.91
2 — 8 d	2.60	0.51	1.33
3 — 5 d	2.51	2.70	6.78
3 — 50 d	2.27	4.42	10.0
4 — 5 d	8.43	—	—
4 — 50 d	0.66	—	—
5 — 5 d	5.80	—	—
10 — 8 d	13.86	—	—
WURDIG (1976)			
10% Alcohol/water, 20 °C	2.7	7.7	21.0
WURDIG (1985)			
Succinate buffer, 10% ethanol			5.4
BERG (1959)			
10% Alcohol/water, 20 °C		1.38	

Approximations of the mean ionic activity coefficient calculated using the Guntelberg equation (BUTLER 1964).

Precipitation kinetics

In the case of potassium bitartrate, nucleation is the initial rate-limiting step until growth is governed by the slower diffusion and surface integration rates (DUNSFORD and BOUTON 1981).

Calcium tartrate

The calcium tartrate data fit third order plots with high correlation coefficients (> 0.95) in the initial 60 min of the first five experiments, as shown in Table 4. This consistent third order kinetic behavior at the beginning of the experiments would indicate that either nucleation or surface integration is the initial rate controlling step in the calcium tartrate crystallization process.

The effect of ethanol on the rate constants can be seen by comparing those of Experiments 1 and 2 with those of Experiments 3 and 4. In each case, ethanol increased

the rate constant by over an order of magnitude (13 times) in the calcium carbonate experiments and by nearly two orders of magnitude (68 times) between the calcium hydroxide experiments.

The differences between calcium carbonate and calcium hydroxide can be seen in Experiments 1 and 3 and Experiments 2 and 4. In Experiments 1 and 3 (water solutions), the rate constant for the carbonate was 5 times that of the hydroxide. This supports the earlier statement that the carbonate enhanced the rate of calcium tartrate precipitation more than hydroxide.

Table 4

Kinetics summary, tartrate, third order plot, 0—60 min

Zusammenfassung der Kinetik-Versuche mit Tartrat, Reaktion dritter Ordnung, 0—60 min

Expt. no.	Slope (rate constant) (L ² /M ² /min)	F-ratio for slope	Correlation coefficient	No. data points
1	4,200 ± 400	91.478	0.968	8
2	55,000 ± 4,000	244.750	0.987	8
3	800 ± 60	159.422	0.978	9
4	54,000 ± 6,000	76.084	0.956	9
5	97,000 ± 3,000	964.894	0.993	15

For Experiments 2 and 4 (ethanol/water solutions), the rate constants were nearly identical. This occurred even though the water experiments indicated that calcium carbonate seemed to be acting seed particle for calcium tartrate. The effect of calcium malate seed crystals on calcium tartrate precipitation can be seen in a comparison of Experiments 3 and 5 (Table 4). The rate constant nearly doubled, indicating the calcium malate particles further enhanced calcium tartrate precipitation.

The calcium tartrate plots after 120 min also appeared to fit a third order kinetic plot (Table 5).

Table 5

Kinetics summary, tartrate, third order plot, 120—240 min

Zusammenfassung der Kinetik-Versuche mit Tartrat, Reaktion dritter Ordnung, 120—240 min

Expt. no.	Slope (rate constant) (L ² /M ² /min)	F-ratio for slope	Correlation coefficient	No. data points
1	2,300 ± 200	173.676	0.997	3
2	34,700 ± 3,000	107.999	0.995	3

Calcium malate

The calcium malate precipitation plots for Experiments 1 through 5 and 10 (Table 6) were not as clear as those of the calcium tartrate. The precipitations appeared to be third or higher order in the first 15 min, indicating a nucleating phase which was strongly dependent on supersaturation.

The effects of ethanol on the calcium malate precipitation can be seen when the plots of Experiments 1 and 2 and Experiments 3 and 4 are compared. There is an increase in the rate constant by a factor of 3 due to the presence of ethanol.

Table 6
Kinetics summary, malate, third order plot, 0-15 min
Zusammenfassung der Kinetik-Versuche mit Malat, Reaktion dritter Ordnung, 0-15 min

Expt. no.	Slope (rate constant) ($L^2/M^2/min$)	F-ratio	Correlation coefficient	No. data points
1	2.7 ± 0.5	25.614	0.963	4
2	8 ± 4	4.852	0.841	4
3	2 ± 1	3.629	0.802	4
4	6 ± 2	8.006	0.894	4
5	10.3 ± 0.9	118.958	0.964	11
10	7.7 ± 0.4	331.782	0.996	4

The data from Experiment 10 was taken from 6 to 15 min due to an initial lag phase.

The differences between hydroxide and carbonate can be seen in Experiments 1 and 3 and Experiments 2 and 4. There was a slight but consistent increase (of 30%) in the rate constant when calcium carbonate was used instead of calcium hydroxide. This is due to a nuclei number or surface area effect in conjunction with the slowing of the rate by ethanol.

The addition of calcium malate seed crystals increased the rate of calcium malate precipitation by 30%, as seen by comparing Experiments 2 and 5. The dramatic effect of seed crystals can be seen by comparing Experiment 10 with Experiments 6, 7, 8 and 9 in Table 2. In each case, little to no calcium malate precipitation occurred, while in Experiment 10 (seeded), the rate constant was $7.7 L^2/M^2/min$ (Table 6). This was similar to $8.0 L^2/M^2/min$ for Experiment 2, where calcium tartrate crystals appeared to act as nuclei for the calcium malate precipitation. However, there was an initial lag phase of 7 min before the crystallization began in Experiment 10. It is notable that the data of the seeded cases (Experiments 5 and 10, Table 7), fit first order plots better than the third order plots. The first order plot of Experiment 10 is shown in Fig. 7. This behaviour indicates that the addition of seed crystals has

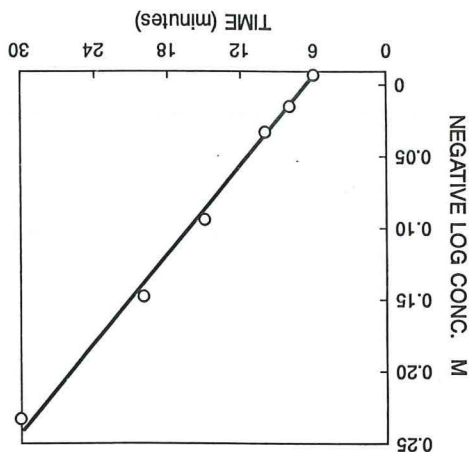


Fig. 7: First order kinetic plot, malate, Experiment 10 from Table 1.
Graphische Darstellung von Malat, Kinetik erster Ordnung, Versuch 10 von Tabelle 1.

shifted the precipitation process to a first order diffusion-controlled mechanism, as the rate limiting step. The later portions (> 120 min) of these two cases appear to be third order plots, though at much slower rates than that of the earlier precipitation process. Additional kinetic studies in juices and wines are needed to determine the effect of sugars, the role of colloids and the optimal calcium source and seed additions.

Table 7

Kinetics summary, malate, first order plot, 0–30 min

Zusammenfassung der Kinetik-Versuche mit Malat, Reaktion erster Ordnung, 0–30 min

Expt. no.	Slope (rate constant) (L ² /M ² /min)	F-ratio for slope	Correlation coefficient	No. data points
5	0.008 ± 0.001	63.237	0.916	14
10	0.0102 ± 0.0004	758.199	0.997	6

The data from Experiment 10 was taken from 6 to 30 min due to an initial lag phase.

Conclusions

There is little evidence to support the existence of a calcium malate-tartrate double salt in these studies.

Calcium tartrate crystallized very quickly in a third order process. Calcium malate crystallized more slowly than the tartrate. In the initial phase, the precipitation was a third (or higher order) process followed later by another third order mechanism.

Seed crystals increased the rate of calcium malate precipitation. Either calcium malate or calcium tartrate can act as seed particles for the malate crystallization.

Ethanol increased the overall rate of precipitation of calcium malate (by calcium carbonate) and calcium tartrate (generally) due to enhanced supersaturation and increased rate constants.

Summary

Calcium salt precipitation was studied in solutions of L(+)-tartaric acid and L(-)-malic acid in both water and ethanol/water mixtures. Calcium tartrate and calcium malate precipitated separately in an interrelated process. Calcium malate crystallization was strongly dependent on seed crystals. Calcium malate and calcium tartrate act as seed particles for calcium malate precipitation. There was no evidence of a calcium malate-tartrate 'double salt' precipitation.

The crystallization kinetics indicate that most of the calcium tartrate precipitated quickly in an initial third order followed by a later third order process. Calcium malate precipitated slowly in two stages like the tartrate but the second stage lasted for many days. The addition of seed crystals shifted the calcium malate precipitation to a first order mechanism. The rate constants were determined for these different stages.

Calcium carbonate provided faster crystallization than calcium hydroxide for both the tartrate and malate precipitations. Ethanol increased the rate of crystallization of calcium tartrate generally and that of the malate with calcium carbonate.

The authors gratefully acknowledge the support of this project by the Stephen Sinclair Scott Memorial Research Fund.

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Eingegangen am 12. 6. 1989

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