Evaluation of Wine Stability to Potassium Hydrogen Tartrate Precipitation

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The effect of several experimental variables (seed amount, seed size, maximum cooling temperature, cooling rate, and stirring) on the measurement of the equilibrium temperature of hydroalcoholic potassium hydrogen tartrate solutions by the seeded polythermal method has been obtained. An experimental protocol optimizing the accuracy of the method is proposed. Because of the accuracy in the results and the short running time (10 minutes), this protocol can be used for testing wine stabilization in industrial process, including continuous stabilization.

KEY WORDS: potassium hydrogen tartrate, wine stability

Whatever the method used to equilibrate the natural potassium hydrogen tartrate (KHT) concentration in wines, it is necessary to test the accuracy of the stabilization. Because wines are multicomponent solutions, several of the methods proposed in the literature of crystal growth for the study of two-component (solute-solvent) solutions cannot be used in this context. In this work ,we discuss the available methods to evaluate the equilibrium temperature (T_e) of wines in relation to precipitation of KHT. The influences of the main experimental parameters affecting the determination of T_e for KHT hydroalcoholic solutions by polythermal method are studied. From these data, the experimental protocol minimizing the testing time is obtained and then applied to dry sherry wines.

The measurement of equilibrium temperature: There are several methods to determine the saturation or equilibrium temperature of a solution (10,11). They are classified and described in the following list, paying special attention to those relevant for the case of wines:

(1) Chemical analysis: This method uses the determination of the pH, [K^+] and [HT^-] ions concentrations (at a given temperature), and from these values, the actual ionic concentration products (ICP) of wines are obtained. Then ICP is compared with the solubility product K_s, which is derived from the equilibrium concentration of modeled KHT hydroalcoholic solutions at the temperature of the test. It is well known that for ideal solutions the region of supersaturation is characterized by ICP > K_s, the equilibrium by ICP = K_s, and finally ICP < K_s is typical for undersaturated solutions. For practical use, these relations have to be modified because the activity coefficients must be known in order to calculate the ionic activity product (IAP) instead of the ICP, since the actual and operative solubility curves and, therefore, the actual K_s values, are derived from IAP values. The calculation of the IAP requires an extensive analytical characterization and a sophisticated calculation program. Moreover, the fact that wines are multicomponent solutions, their equilibrium concentrations versus temperature curves cannot be modeled by a single set of data obtained from hydroalcoholic solutions of the same alcoholic degree. This method has been proposed by Berg and co-workers (1,2) and is currently used in the literature on wine stabilization. However, this practice does not appear to be capable of quick and practical evaluation of the risk of precipitation in continuous stabilization.

(2) Toepler's method (10): This method is based on the detection of the concentration pattern around the interface of a single crystal immersed in the sample. In practice, the equipment consists of an optical system able to reveal the concentration pattern created by either crystal solution or crystal growth. Such patterns appear from the difference in refractive index of the solution layers around the crystal provoked by the input (growing crystal) or output (dissolving crystal) of growth units to the crystal face, which disappear at equilibrium temperature. Such a method requires the continuous assistance of an operator unless an automatic image analyzer is used. This arrangement has not been yet reported in the literature.

(3) Physical property measurement: Another common method for evaluating the concentration of a solution and its equilibrium temperature is to measure a physical property *P*, such as density, viscosity, conductance, or refractive index and then to compare it with the available data on the variation of *P* with equilibrium concentration at different temperatures (10,11). Because of the multicomponent character of the wines, it is impossible to use a general solubility curve. The same problems occur for other several methods proposed for the characterization of two-component (solvent-solute) solutions, such as the measurement of dry residues and boiling point elevation.

(4) Polythermal method: This procedure was proposed by Nyvlt (11) and is better described by using the

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Acknowledgements: Work performed under financial support from CICYT project nº PA86/0119. We acknowledge Juan Gómez from Osborne S.A. for the supply of wine samples and the values of their analytical data.

This research was conducted at University of Granda, Spain.

Manuscript submitted for publication 9 January 1991.

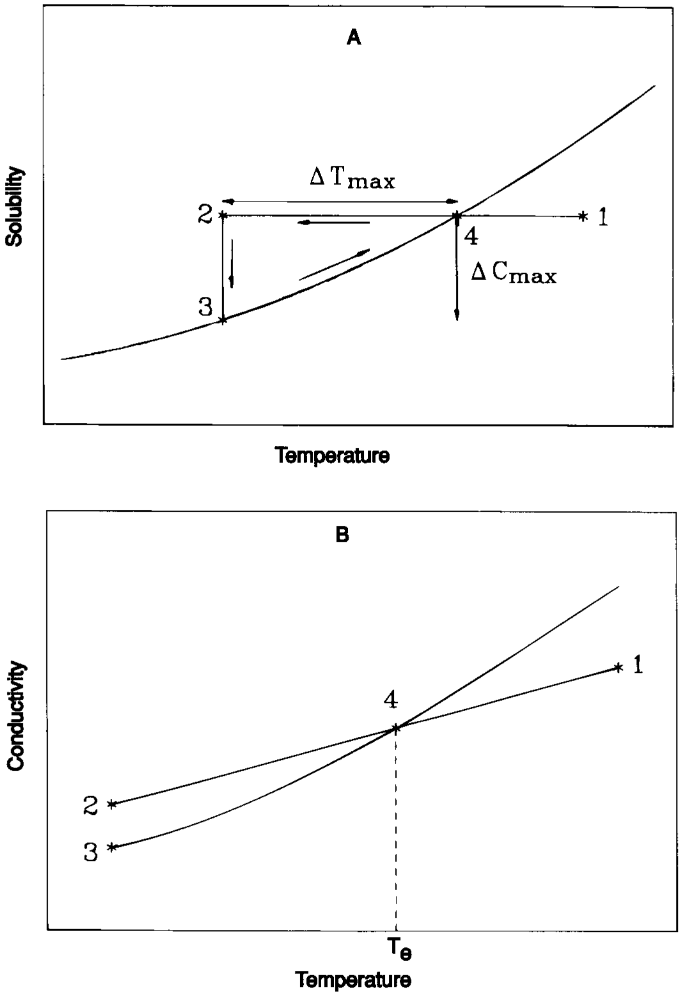

Fig. 1. The polythermal method for the evaluation of the equilibrium temperature of two-components solutions. ***(a)*** The solubility versus temperature plot: *(1)* Starting solution. *(2)* Solution starts to precipitate on the superequilibrium curve. *(3)* After precipitation the solution is on the equilibrium curve. *(4)* The solution is at equilibrium temperature T_e, the point at which the last crystals disappear. ***(b)*** Behavior of the conductivity along the paths of Figure 1a in a conductivity versus temperature plot.

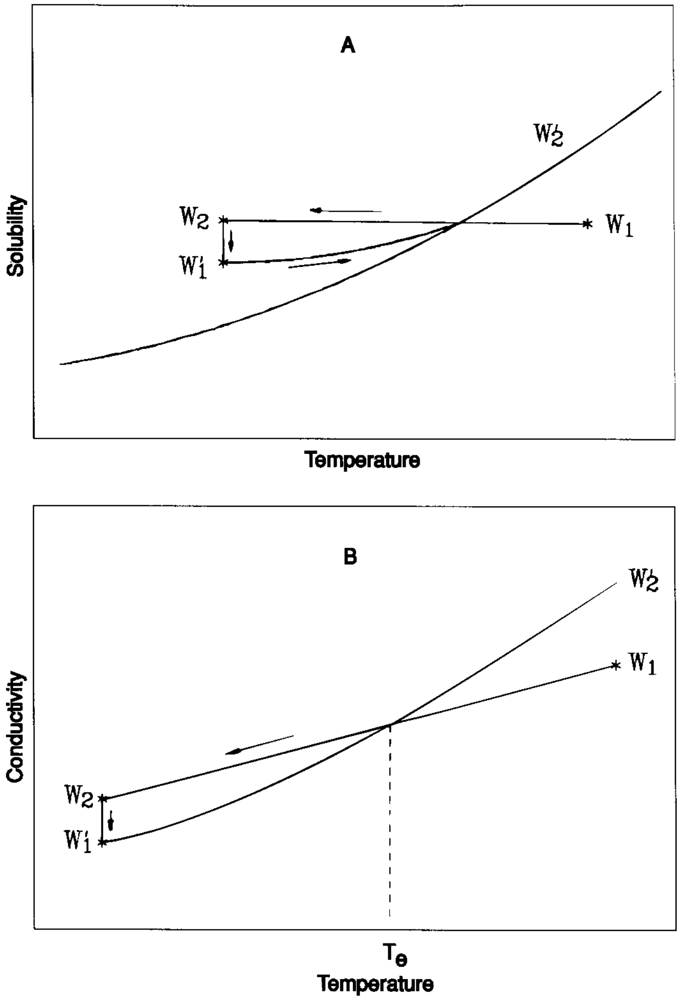

Fig. 2. The application of the polythermal method to test the equilibrium temperature of wines. ***(a)*** The solubility versus temperature plot: (W_1) Starting sample. (W_2) Sample is seeded in the metastable zone. (W'_1) Sample after precipitation of potassium hydrogen tartrate. (W'_2) Sample after heating until the starting temperature. ***(b)*** Behavior of the conductivity along the paths of Figure 2a in a conductivity versus temperature plot.

Ostwald-Myers diagram to show the sequence of events and the nature of the method (see Fig. 1a). The temperature of the sample is measured, and then it is cooled down quickly to the labile zone of the diagram, *i.e.*, until a crystal precipitate appears. In this way, the maximum undercooling ΔT_{max} and the width of the metastable zone ΔC_{max} is obtained. The sample is slowly heated while temperatures are continuously recorded. The temperature at which the last crystals disappear is the equilibrium temperature. If the solubility curve of the substance is known, the actual concentration of the solution can be evaluated from these data. As Nyvlt pointed out, the visual detection used in the classical polythermal method can be changed by any of the chemical properties directly related to the equilibrium temperature of the solution. In fact, any of the properties listed in (3) can be used. Their use is restricted by the available data on the variation of the property with solubility and, in general, with concentration. We have previously demonstrated (6) that the best method to record the salting-out and its reverse process is the noise associated with the intensity of the reflected light. The second most sensitive property is conductivity, which can be used in this case. The expected behavior of conductivity along the path 1-4 in Figure 1a is shown in Figure 1b.

The polythermal method loses confidence when the rate of change of solubility with temperature is very high. For KHT hydroalcoholic solutions or wines this is not the case ($\delta c/\delta T = 3.7\ 10^{-4}$ mol/°C), and therefore, such a method appears to be very appropriate. The only disadvantage arises when the large width of the metastable zone of KHT in wines is considered. In terms of temperature, typical ΔT_{max} is about 25°C and in terms of concentrations ΔC_{max} is about 1.74 g/L. This means that, in order to attain the labile zone, the temperature must be lowered below 0°C, which introduces, not serious but time-consuming and costly, technical problems in the use of this method. Moreover, for ready-to-bottle wines, it is expected that the maximum undercooling will be greater than the freezing temperature, which in general is considered to be one degree Celsius lower than half of the alcoholic degree. Therefore, the experimental run requires an extensive waiting time for precipitation.

The combination of conductivity and polythermal method has been proposed in wine literature in a slightly different way than the classical polythermal method (7,8,9,12,14). This variation requires two consecutive cooling-heating baths but avoids the use of negative Celsius temperatures. This method takes advantage of the large metastable width zone of KHT and assumes that under conditions of no precipitation, temperature and conductivity of stable or metastable solutions fit a linear relationship. The method consists in the measurement of specific conductivity (Λ) versus temperature for the wine tested (W) in the metastable zone (for instance, between 20°C to 4°C). The solution then is seeded with a certain amount of KHT (W') and again the variation of conductivity with temperature is continuously recorded from 4°C to 20°C. In Figure 2a, we have plotted the paths followed by the two experiments in the Ostwald-Myers diagram. The variations of conductivity in the two paths are displayed in Figure 2b. When $\delta\Lambda = \Lambda(W) - \Lambda(W')$ is plotted versus T, a curve is generated in which the value $\delta\Lambda = 0$ is expected to be the temperature of saturation (Fig. 3). The reason is clear if one considers the plot of Figure 2b. For practical purposes, it can be considered that $\Lambda(W)$ has a linear relationship with temperature. Because W is a solution which is metastable or undersaturated in the range of temperature evaluated, the number of active ions in solution is constant. Therefore, the variation in conductivity is exclusively devoted to the effect of temperature. On the contrary, W' is a metastable solution to which a large amount of KHT was added, and therefore, the nucleation barrier was drastically diminished and KHT precipitation occurred immediately; consequently, concentration and conductivity decrease. Later, on the heating path, concentration and conductivity increase along the solubility curve and will intersect the previous W_1 - W_2 curve at some point. It is assumed that the temperature at which the difference in conductivity is zero will be the equilibrium temperature (T_e) of the wine tested. Unfortunately, this last assumption is only correct if the system is allowed to move on the equilibrium curve. To accomplish this, it will be necessary: *(a)* to wait for an isothermal drop to equilibrium concentration after seeding (W'). This waiting time depends on the experimental conditions (3,4,5); *(b)* To use a heating rate of W' lower than the dissolution rate of the crystals in order to avoid large deviations from equilibrium.

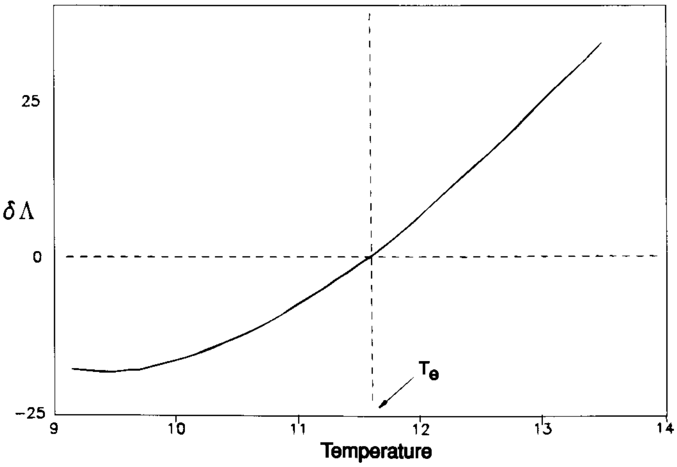

Fig. 3. The difference in conductivity in front to temperature, between seeded and unseeded hydroethanolic solutions of potassium hydrogen tartrate.

Both requirements are time consuming, and therefore, they present problems in the industrial use of the test, mainly in continuous stabilization systems. Therefore, we have performed several experiments in order to find an experimental protocol minimizing the testing time and providing a high accuracy in the evaluation of T_e.

Materials and Methods

KHT solutions were made from KHT (Probus PRS), ethyl alcohol absolute (Probus PRS), and distilled water. KHT hydroalcoholic solution saturated at 11.05°C were prepared by adding 1.5596 g of KHT to 1 L of a 16% in volume hydroethanolic solution. Four different sizes ϕ of KHT particles were used in the experiments : *(a)* $\phi < 50$ µm; *(b)* $50 < \phi < 100$ µm; *(c)* $100 < \phi < 200$ µm; and *(d)* $200 < \phi < 500$ µm. Particle size distributions were obtained by sieving and by a light-scattering particle sizer. An open reservoir containing the solution was placed in a thermostated bath with continuous stirring. The temperature and conductivity of the solution as well as the bath temperature were continuously recorded and later digitized and computer-stored. Once the solution temperature of 20°C was reached a couple of temperature and conductivity values were obtained. The bath temperature then was adjusted to a value corresponding to a maximum cooling temperature (MCT = 9°C, 6°C, and 3°C), and later the solution was seeded with a concentration of KHT particles ([s] = 2, 4 and 8 g/L) and heated to 15°C. The temperature and the conductivity were continuously recorded during the entire process. The data are the statistical average of a representative number of independent measurements. They are computed by fitting a minimum of one thousand temperature-conductivity couples to a polynomial curve. The estimated error in the measurement of the equilibrium temperature is ± 0.05°C. The effect of particle size (ϕ), maximum cooling temperature (MCT), stirring [S = mechanical stirring (S_m) or ultrasounds (S_u)], and heating rate (H_1, H_2 or H_N) were tested with the same experimental protocol described above. The selected set of values of the experimental variables was later applied to the determination of the equilibrium temperature of dry sherry wines.

Results and Discussion

The effect of heating rate was tested in three experimental runs, two with controlled heating rates of H_1 =

3 °C/min and H_2 = 0.2 °C/min, and one with the natural heating law ($H_N \approx$ 0.5 °C/min). For [s] = 8 g/L; size diameter $\phi < 50$ µm; § = S_m and MCT = 9°C, the following T_e, with the estimated error of ± 0.05 °C, were obtained:

H_1 (3°C/min) .... T_e = 11.59
H_N (0.5°C/min) .... T_e = 11.10
H_2 (0.2°C/min) .... T_e = 11.04

For the above conditions, but using in all cases natural heating, the effect of maximum cooling temperature is as follow:

for MCT = 3°C.............. T_e = 11.54
for MCT = 6°C.............. T_e = 11.52
for MCT = 9°C.............. T_e = 11.10

For the above conditions, with MCT = 9°C, the effect of crystal size (µm) is as follow:

for $\phi <$ 50 ....T_e = 11.10
for 50 < ϕ < 100 .... T_e = 11.47
for 100 < ϕ < 200 .... T_e = 10.78
for 200 < ϕ < 500 .... T_e = 10.36

For the same experimental conditions (MCT = 9°C; f < 50 µm; H_N and § = S_m), the effect of the amount of seeding is as follows:

for [s] = 8 g/L .... T_e = 11.10
for [s] = 4 g/L .... T_e = 11.39
for [s] = 2 g/L .... T_e = 11.63

The effect of ultrasonic energy (S_u) was also tested. The results obtained for [s] = 8 g/L, ϕ < 50 µm, and MCT = 9°C are:

with H_1 and § = S_m .... T_e = 11.1
with H_1, § = S_m and S_u ..... T_e = 11.3
with H_N, § = S_m and S_u ..... T_e = 11.5

These results show how the evaluation of T_e by the polythermal method can be affected by the experimental conditions. The best accuracy in the determination of T_e is obtained with an experimental protocol assuring that, along the heating path, the solution moves on the solubility curve. This requires too much time to be used in industry. Minimizing the waiting time for a quicker method will lead to consideration of the kinetic aspects of the problem.

First, we will need to avoid the drop to equilibrium temperature. This will allow a higher heating rate without the risk of moving the solution into the region of undersaturation. The better results obtained at higher absolute values of MCT are explained as the effect of the lower drop of concentration when the solution is seeded.

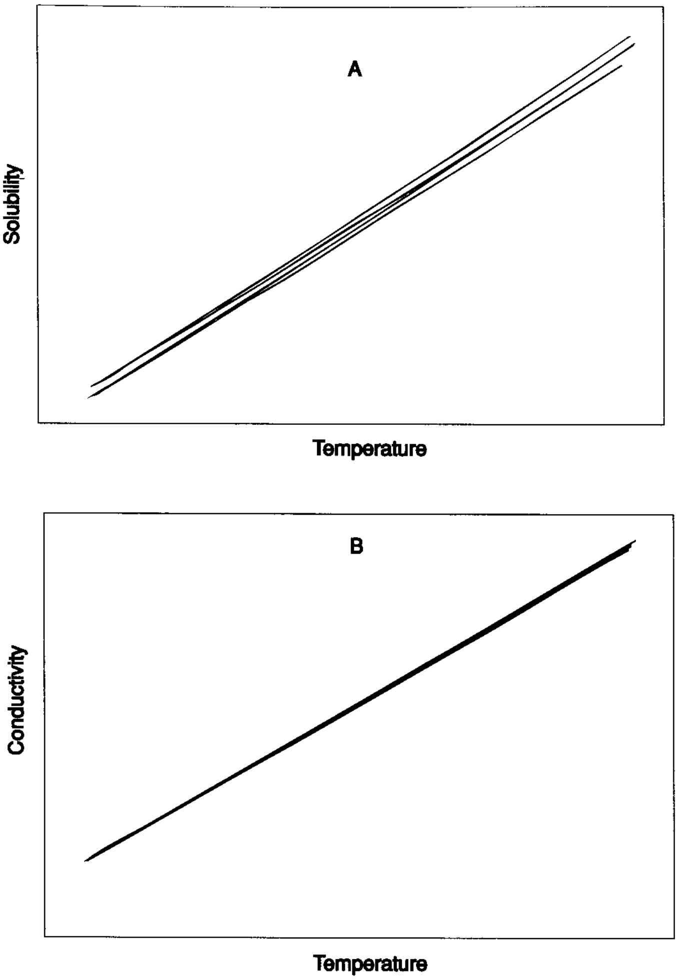

Fig. 4. Conductivity versus temperature for two consecutive cooling and heating paths of unseeded ***(a)*** KHT 16% hydroethanolic solutions and ***(b)*** KHT water solutions.

In fact, the important point is to assure the heating rate to be lower that the dissolution rate in order to avoid departures from the actual T_e values. The dissolution rate increases by decreasing the particle size and increasing the seed concentration, *i.e.*, increasing the specific surface of the KHT seeds. Mechanical agitation is thought to increase the dissolution rate, but the effect of ultrasound seems to enhance precipitation better than dissolution. We have observed that 8 g/L is the better seed concentration. Higher seed concentrations are not useful because a larger concentration drop provoked by precipitation is not desirable. We have found an anomalous behavior for particle sizes between 100 and 500 microns. This is due to the fact that the use of an open reservoir allowed alcohol evaporation and water condensation to occur during the testing procedure. Because of the lower concentration drop at larger seed size, such an effect is especially evident under these conditions. This was determined by a series of experiments in which unseeded KHT hydroalcoholic solutions were subjected to successive cooling and heating paths (Fig. 4a). The deviations observed cannot be explained by the time-delay of the conductivity cell to obtain a stable value, because the rate of cooling was higher than the heating rate. Moreover, KHT water solutions were tested in the same way, and as seen on Figure 4b, no such deviations were found. The same test was performed after covering the KHT solution with a thin film of oil, and no deviations were found in the behavior of the conductivity. Therefore, the effect of

Table 1. Evaluation of T_e and ICP for dry Sherry wines (16% alcohol by volume). *(1)* Unhanded wine. *(2)* Wine filtered and clarified with egg albumin. (3 through 7) Ready to bottle stable wines after classical cooling stabilization. [K] and [H_2T] in mol/L and T_e in Celsius degrees.

	$[K^+]\ 10^2$	$[H_2T]\ 10^3$	pH	% HT^-	ICP 10^5	T_e
1	2.1024	15.6306	3.19	54.9	18.0412	21.9
2	2.1024	15.2575	3.20	55.4	17.7710	21.8
3	1.3325	9.0279	3.09	50.0	6.01511	11.2
4	1.2481	9.1545	3.07	49.0	5.5988	9.8
5	1.2926	8.8414	3.07	49.0	5.5957	9.7
6	1.3453	9.7741	3.07	49.0	6.4433	11.5
7	1.3453	8.9680	3.06	48.5	5.8515	10.7

alcohol evaporation and water condensation must be taken into account when using this method. We have also observed that under appropriate values of the experimental parameters, a natural heating procedure led to experimental results not enhanced by the use of controlled lower heating rates.

We propose an experimental protocol using the following conditions: maximum cooling temperature = 2-3°C lower than the suspected T_e; seed concentration = 8 g/L; heating rate = Natural Newton law; particle size < 50 µm; stirring = mechanical (no ultrasounds) high energy.

The expected value of T_e can be obtained by a first evaluation using the above conditions with a maximum cooling temperature of 6°C (it is not usual for wines to found a T_e value lower than 6°C).

The above experimental protocol was used to test dry sherry wines, previously characterized. The results obtained are displayed in Table 1. As can be observed there is a direct correlation between the values of ICP - calculated by the method proposed by Berg (1) and T_e obtained by our experimental protocol.

Conclusions

The accurate evaluation of T_e can be a routine method to test stabilization procedures in wineries. If the values of T_e of a particular type of wine is known to be well-equilibrated, the evaluation of T_e after each stabilization session provides an easy, quick, and low cost test for the risk of precipitation. Even in those cases where continuous stabilization is the selected procedure, this fast and accurate method can be used.

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