Salt Effect on the Vapor/Liquid Equilibrium of Wine

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The effect of $CaCl_2$, $CoCl_2$, $CuCl_2$, and NaCl on the vapor/liquid equilibrium of the main constituents of wine has been studied in a concentration range of 0 to 9.2 mol/kg $CaCl_2$, 0 to 1.0 mol/kg $CoCl_2$, 0 to 4.9 mol/kg $CuCl_2$, and 0 to 4.4 mol/kg NaCl. It was observed that as the concentration of salts in wine increases, the equilibria shift toward a vapor phase richer in volatile components, increasing the separation facilities. Also, a possible catalytic effect has been found for the $CuCl_2$ to detect an increased concentration of methyl and ethyl acetates in vapor phase, diminishing the acetaldehyde concentration.

Spain, owing to its wine surplus, is a producer of ethyl alcohol. Part of this alcohol is consumed by the wine industry itself in raising the alcohol content of wines. This requires rigorous control of the components accompanying the ethanol, which means that in some cases, the concentration of some of them must be reduced or even eliminated.

Another part of the surplus alcohol is used as fuel, although there are prospects of transforming it into anhydrous alcohol for use as vehicle fuel or to improve gasolines. This requires highly versatile installations, which are difficult to obtain for mechanical and financial reasons. This, combined with problems arising from the energy crisis, means that a large number of distillation plants are lying idle because they are not profitable and the investment needed to reconvert them would be too heavy.

There is a need for new operating methods which allow greater separation in the distillation plants with lower energy consumption. These methods include the addition of electrolytes to the raw material which alter the composition of the vapor/liquid equilibrium, thus obtaining greater separation among the components (2,3). In some azeotropic systems, the equilibrium can be broken, leading to greater separation with corresponding energy savings (1).

The aim of the present work was to study the effect of $CaCl_2$, $CoCl_2$, $CuCl_2$, and NaCl on some of the main components of wine, such as ethanol, acetaldehyde, methyl and ethyl acetates, methanol, *n*-propanol, *i*-butanol, *n*-butanol, and *i*-amyl alcohols, in the vapor/liquid equilibrium.

The reason for using these salts lies in the expected enhancement of the volatility of some of the abovementioned components, which would facilitate their separation. Again, these components were considered of particular interest for distillation processes since they normally accompany ethanol in top products and are thus denominated "congeners".

Materials and Methods

An equilibrium still was used, as illustrated in Figure 1. This apparatus permits the determination of the concentrations of the wine components in equilibrium in the liquid and vapor phases, rectification being prevented as the two currents follow different routes. The equilibrium is detected when the temperature of the vapor (measured on the thermometer T) remains constant. One hour after reaching equilibrium, the samples were taken. These were cooled by passing through coolant (C) (to prevent any escape of volatiles) by way of the three-way valve (V), then analyzed. All experiments were conducted in duplicate.

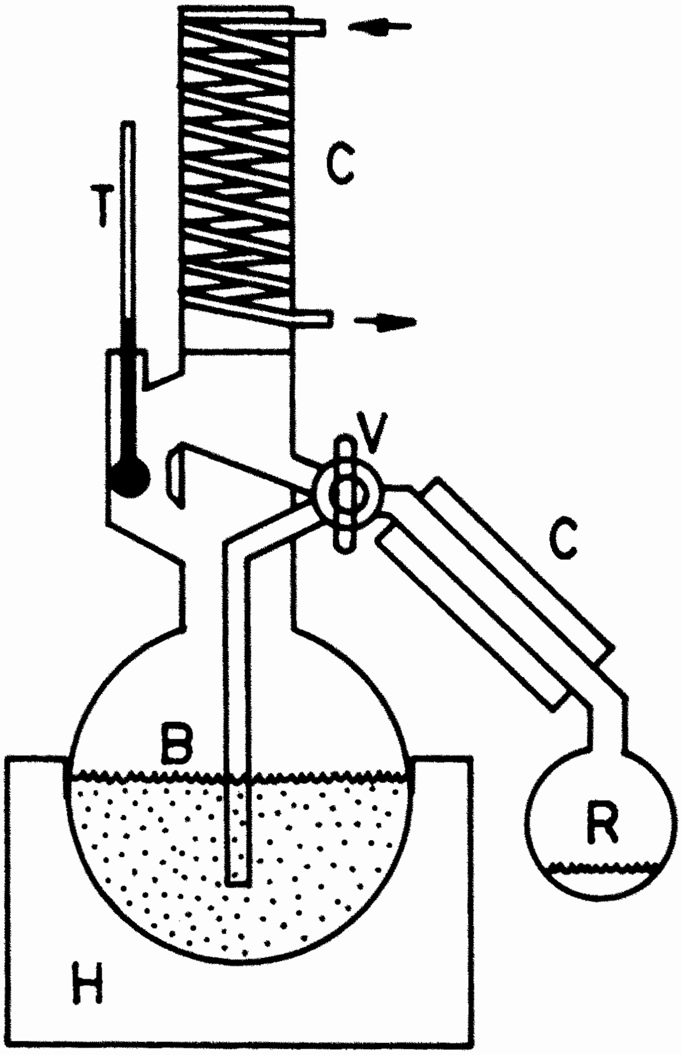

Fig. 1. Equilibrium still. H - heater, B - boiler, T - thermometer, C - coolants, V - three-way valve, R - receiver.

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The composition of the samples was determined using a Perkin-Elmer gas chromatograph model 881. The chromatographic peaks were quantified with a Hewlett Packard integrator model 3390A. A 2 m × 1.8 mm i.d. stainless steel chromatographic column was used. The stationary phase was composed of Carbowax 1500 supported on chromosorb 80 - 100 mesh.

Analytical conditions were as follows: dual flame ionization detector; injector temperature, 200°C; detector temperature, 150°C; oven temperature, 90°C; carrier gas, nitrogen; flow rate, 30 mL per minute; and internal standard, 2-pentanol.

The raw material used was sherry-type wine, whose characteristics and composition (with reference to ethanol and its congeners) are expressed in Table 1, along with those of its vapor in equilibrium, which will be used later for comparison. Most noticeable is the enormous difference between the concentrations of ethanol and those of the other congeners, the former being *ca* 1000 times greater.

Table 1. Compositions of wine used as raw material and its vapor in equilibrium.

Component	Concentration (m*M*)	
	Wine	Vapor
Acetaldehyde	7.74	38.16
Methyl acetate	0.03	0.59
Ethyl acetate	0.59	12.22
Methanol	1.72	4.84
Ethanol	2.80×10^3	11.18×10^3
n-Propanol	1.48	4.91
i-Butanol	0.78	6.21
n-Butanol	—	—
i-Amyl alcohols	2.54	20.02

The salts used were analytical grade $CaCl_2$, $CoCl_2$, $CuCl_2$, and NaCl.

Solubility was determined considering the quantity of water added with the hydrated salt, so that the salt concentration in the wine is expressed as moles of anhydrous salt per kilogram of solvent (wine plus water from salt hydration).

The salts $CaCl_2$ and $CoCl_2$ were chosen for their known solvation capacity (5,7). In principle, this should upset the vapor/liquid equilibrium of the components of the wine as the amount of water available in the solution diminishes.

$CuCl_2$ was studied because many industrial distillation apparatuses are made of copper, which is attacked and dissolved during the operation resulting in the presence of this salt, albeit in small proportions, during the distillation process. In addition, the solvation effect of $CuCl_2$ is well known (4), so that along with the possibility of its acting as a catalyst during the process (8), it was an attractive subject of study.

Finally, NaCl was used because its low cost makes it interesting from the industrial viewpoint, especially in southern Spain.

Results and Discussion

Effect of the salts on ethanol equilibrium: Since, apart from water, ethanol is the major and most important component of wine, the first study was of the effects of the salts on its vapor/liquid equilibrium. Figure 2 shows the ethanol concentration in the vapor phase in equilibrium with the liquid phase, as against the salt concentration in the wine, for the four salts used. It can be deduced from this figure that the effectiveness of ethanol separation in wine, taken as the ethanol concentration in the vapor phase at maximum concentration of salt in the wine, is similar for $CaCl_2$, $CoCl_2$, and NaCl (14 mol/L) and lesser for $CuCl_2$ (13 mol/L). The levels reached agree with those found for the hydroalcoholic mixtures with the same composition as the wine (molar fraction 0.06) saturated with the same salts (4,5,6,7),

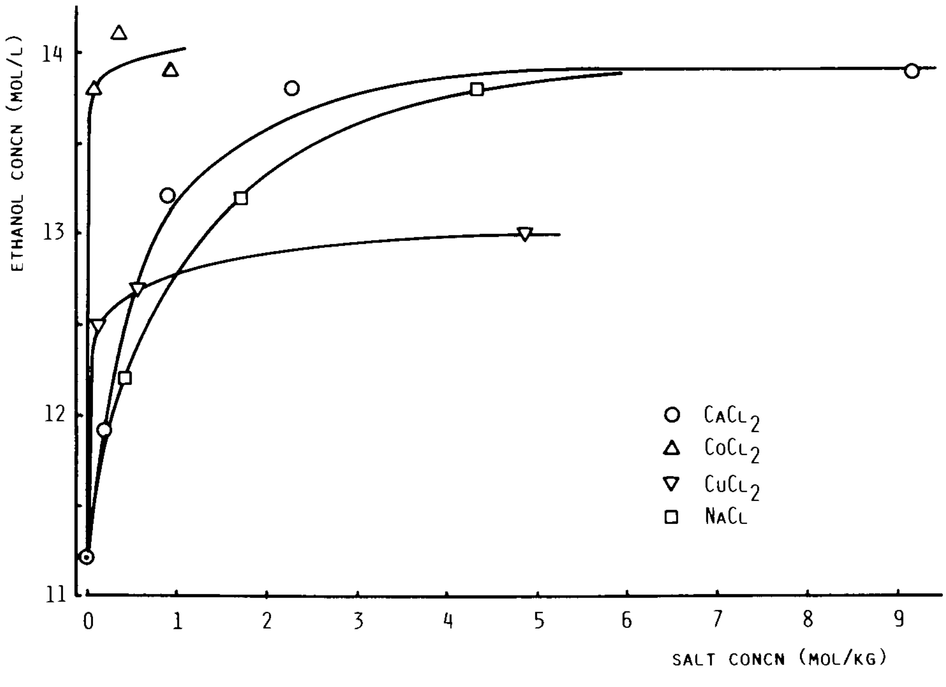


Fig. 2. Ethanol concentration in the vapor phase *vs.* salt concentration in the liquid phase.

which would indicate that it is unnecessary to reach saturation of the salts to achieve maximum separating efficacy.

To express the experimental data found to the vapor/liquid equilibrium of ethanol in the presence of salts, the following equation can be used:

$$y = a + b \bullet \ln x \qquad \text{(Eq. 1)}$$

where y = the concentration of ethanol in equilibrium in the vapor phase (expressed in mol/L), x = the concentration of salt in the boiling liquid (expressed as mol/kg of solvent), and a and b = the particular coefficients of each salt.

Table 2 shows the values of the coefficients a and b in Equation 1 for each of the salts and the logarithmic curve adjustment, r, calculated from the experimental data. The physical meaning of coefficient a is the concentration of ethanol in the vapor phase where the concentration of salt in the wine equals 1 mol/kg, and it denotes the separating power of the salt. The coefficient b denotes the effect produced by the increase in concentration of the salt in the liquid phase on the ethanol content of the vapor.

In order to determine the accuracy of Equation 1, the data of ethanol concentration in the vapor phase calculated for salts at saturation in wine have been compared with the experimental data found for hydroalcoholic mixtures with ethanol compositions the same as that of wine and saturated with the same salts (4,5,6,7). The results of this comparison also appear in Table 2.

Table 2. Calculated and experimental (4,5,6,7) ethanol concentrations (*M*) in vapor phase for liquid saturated with salts.

Salt	Coefficients of Eq. 1 a	b	r	Calculated using Eq. 1	Experimental
$CaCl_2$	13.02	0.664	0.94	14.79	15.13
$CoCl_2$	13.93	0.020	0.95	13.97	13.91
$CuCl_2$	12.64	0.200	0.96	13.06	13.20
NaCl	12.77	0.710	1.00	14.12	14.37

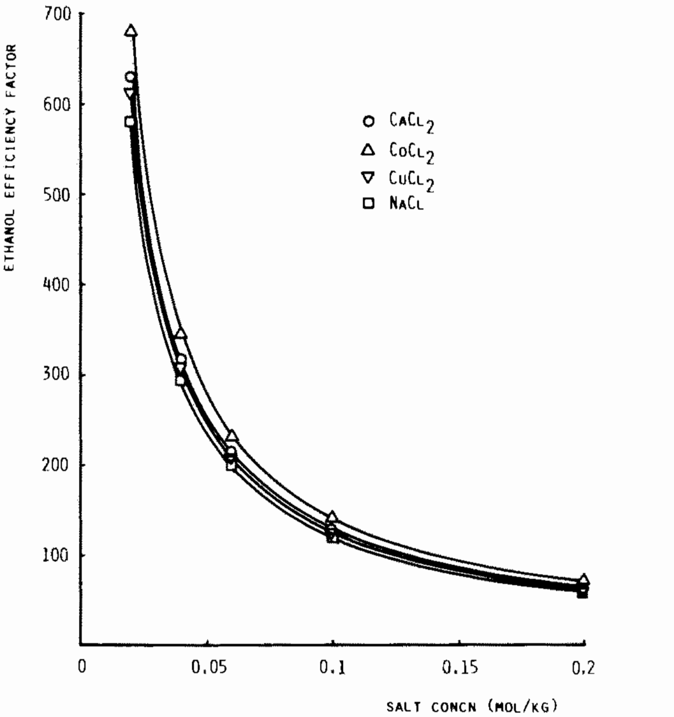


Fig. 3. Efficiency factor of ethanol *vs.* salt concentration in the liquid phase.

The efficiency factor of ethanol separation is defined as its concentration in the vapor phase (mol/L) divided by the concentration of salt in the wine (mol/kg). Figure 3 shows this efficiency factor as against salt concentration. It can be observed that the efficiency factor increases in the direction $CoCl_2 > CaCl_2 \simeq CuCl_2 > NaCl$. This indicates that to obtain a given ethanol separation, the required concentration of salt in the wine is least for cobalt salt, somewhat greater for calcium and copper salts, and greatest for sodium salt.

On the other hand, the difference in magnitude of the efficiency factors, and hence the separation obtained, increases as the concentration of salts in the wine decreases. This is a very important factor in regards to cost.

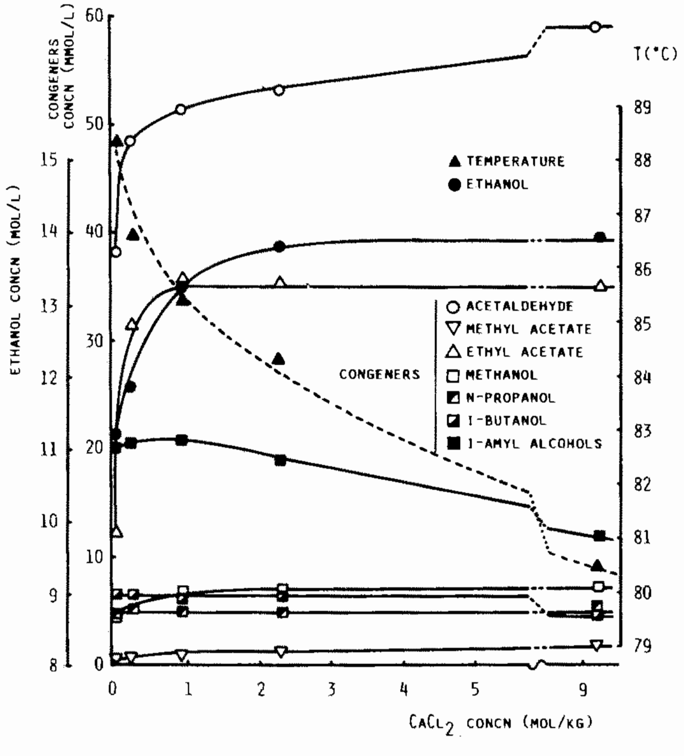


Fig. 4. Temperature, ethanol concentration, and congeners concentration in the vapor phase *vs.* $CaCl_2$ concentration in the liquid phase.

Since the vapor in equilibrium with the wine is progressively enriched in ethanol as the concentration of salts present increases (becoming poor in water), the temperature of equilibrium should decrease as a consequence of the greater volatility of ethanol (Fig. 4, 5, 6, 7). Nevertheless, it should be noted that although the expected decrease does occur, it is not the same for all the salts, since these upset the vapor/liquid equilibria of the other congeners in the wine in a different way.

Effect of the salts on the equilibrium of the congeners: After observation of the effect of the different salts on ethanol equilibrium, the next step was to

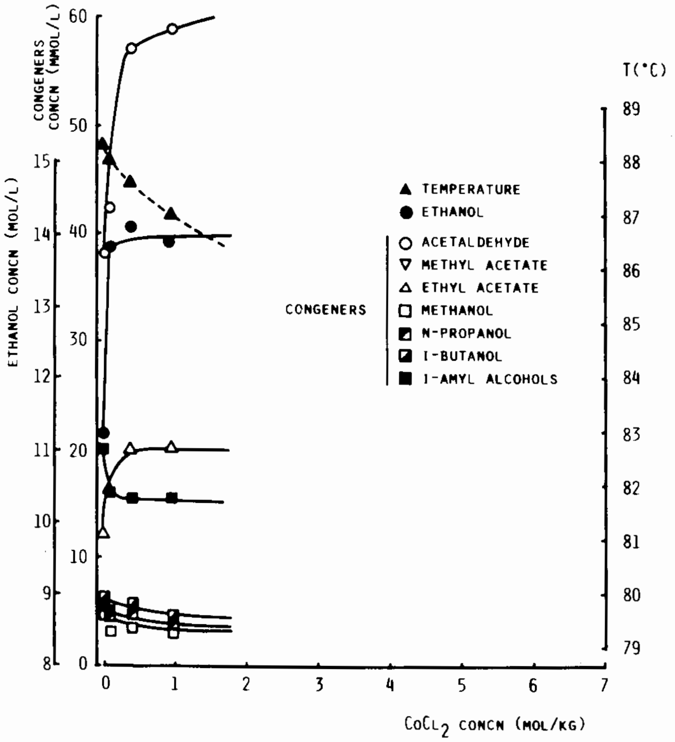


Fig. 5. Temperature, ethanol concentration, and congeners concentration in the vapor phase *vs.* $CoCl_2$ concentration in the liquid phase.

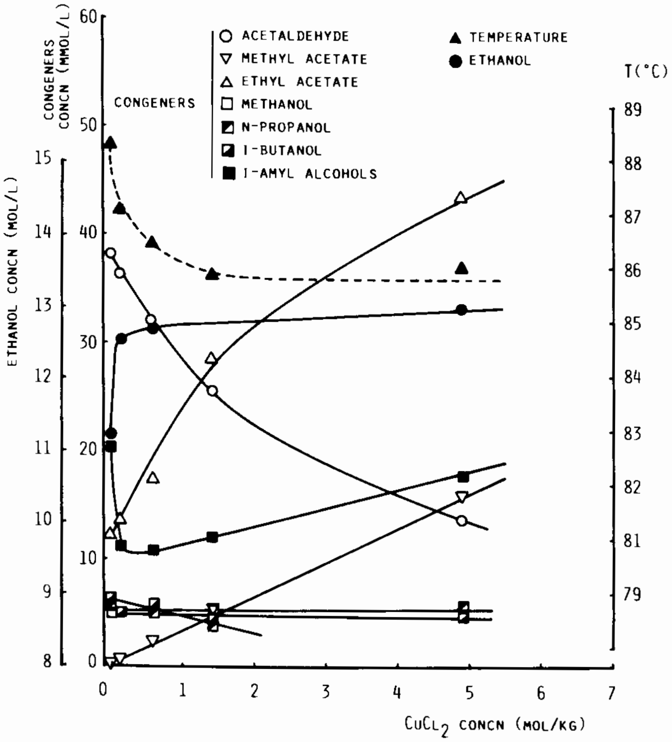


Fig. 6. Temperature, ethanol concentration, and congeners concentration in the vapor phase *vs.* $CuCl_2$ concentration in the liquid phase.

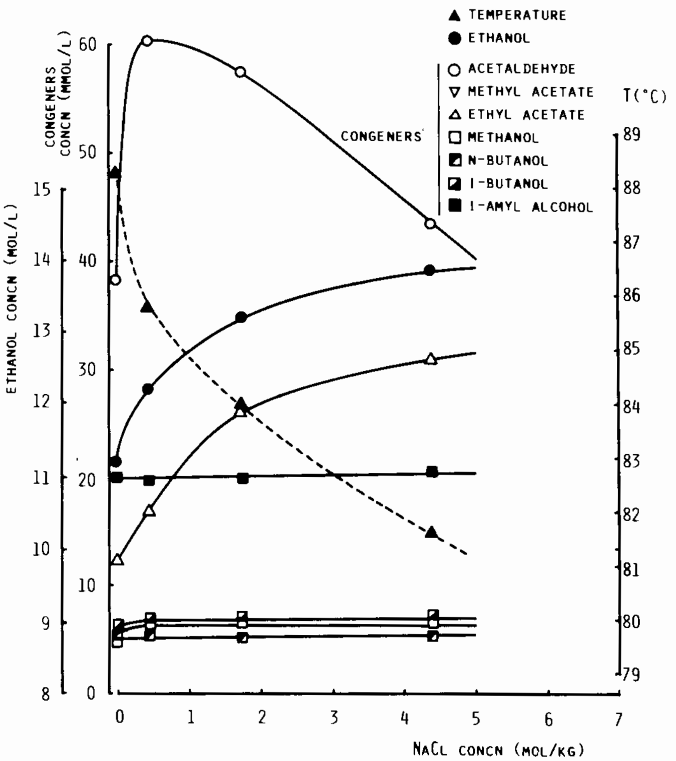


Fig. 7. Temperature, ethanol concentration, and congeners concentration in the vapor phase *vs.* NaCl concentration in the liquid phase.

study the effect wrought on the vapor/liquid equilibria of the other congeners.

The experimental data can be seen in Figures 4, 5, 6, and 7, which show the concentration of the congeners (mmol/L) as against the concentration of each salt in the wine (mol/kg). On the basis of these data and by comparison with the data given in Table 1 for the vapor in equilibrium with the wine without salt, the following can be deduced.

In the case of $CaCl_2$, the concentrations of acetaldehyde, methyl acetate, ethyl acetate, and methanol increase along with the salt concentration in the liquid phase, following an evolution similar to that of ethanol (with the exception of ethyl acetate which, from a salt concentration of 1 mol/kg onwards, does not vary owing to its exhaustion).

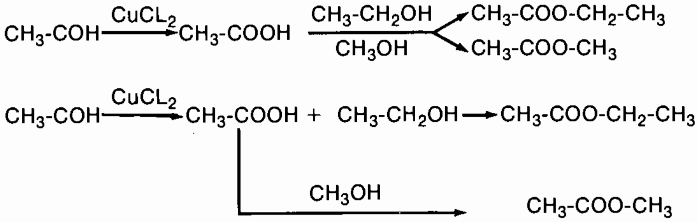
The equilibria of the less volatile congeners (such as *n*-propanol and *i*-butanol) are not affected by the salt, while in the *i*-amyl alcohols, there are slight decreases in concentrations when salt concentrations increase. These effects may be due to an increase in the solubility of those components in the liquid phase as the salt is solvated by the water, thus reducing the presence of water in the medium so that this phase tends toward a higher alcohol content in which they are more soluble.

With $CoCl_2$, behavior is similar to that found with $CaCl_2$ except that the highest levels of congener concentration in the vapor are attained with noticeably lower salt concentration (0.4 mol/kg *vs.* 2 to 3 mol/kg) (Fig. 5). Following an evolution similar to that of ethanol, the concentration of the more volatile congeners varies with the concentration of $CoCl_2$ in the wine.

$CoCl_2$ also produces a slight fall in the concentration of the medium- and low-volatility congeners (*i.e.*, within the range of methanol-*i*-amyl alcohols). This is undoubtedly due to the high power of cobalt to solvate and form coordination compounds; as a result, its separating efficiency is far greater.

When the salt dissolved in wine is $CuCl_2$, there are two effects which can be considered peculiar (Fig. 6): 1) the progressive disappearance of acetaldehyde from the vapor phase in equilibrium with the liquid phase as the concentration of $CuCl_2$ increases in the wine; and 2) the progressive increase in the levels of methyl and ethyl acetates in the vapor, reaching levels higher than those obtained if all the wine content in these components were to pass on to the vapor phase (2.4 and 35 mmol/L, respectively) and clearly indicating that formation of these two congeners must take place in the process.

These facts can be explained by supposing that $CuCl_2$ acts on the acetaldehyde in the boiling liquid, transforming it into the corresponding acetates. This transformation would be in direct proportion to the presence of salt in the medium and could work in two ways:



The first is an oxidation reaction where for each mole of acetaldehyde that disappears, a mole of acetic acid is formed and is subsequently esterified with ethanol or methanol, giving the corresponding acetates in concentrations proportional to their respective formation constant.

The second is a self-oxidation/reduction reaction in which two moles of acetaldehyde are consumed to form one of acetic acid and another of ethanol. Immediately after, the acid is esterified.

Since most industrial distillation apparatuses are made of copper, which is attacked by SO_2 dissolved in wine to generate Cu^{2+} ions, the foregoing may explain why the top products of distilling processes show such high methyl and ethyl acetate contents.

Again, as occurs with $CaCl_2$, medium-volatility components are not affected by the presence of $CuCl_2$. On the other hand, *i*-amyl alcohols evolve significantly. In fact for low $CuCl_2$ concentrations, the *i*-amyl alcohols content of the vapor falls as the salt concentration rises as a result of the increased solubility of this component in a more water-poor liquid medium (as occurred in the case of $CaCl_2$). However, for $CuCl_2$ concentrations higher than 0.3 mol/kg, the effect was inverted. At these salt levels, the concentrating effect of the compound in the medium is stronger than the effect of heightened solubility and so there is an increased presence of *i*-amyl alcohols in the vapor.

The nature of the effects produced by the presence in the wine of NaCl on the composition of the vapor phase in equilibrium depends on the concentration of the salt (Fig. 7).

For concentrations of this salt below 0.5 mol/kg, the concentration of the more volatile congeners increases along with the concentration of this salt in the liquid phase; thus, the salt's behavior is similar to that of $CaCl_2$ and $CoCl_2$. On the other hand, for concentrations of the salt above the value stated, increases in salt concentrations lead to a fall in the levels of acetaldehyde in the vapor, giving way to increased concentrations of ethyl acetate with no perceptible presence of methyl acetate. Thus, within this range of concentration, NaCl behaves like $CuCl_2$, that is to say like an esterifying salt but selective in character.

Regarding the rest of the congeners, the behavior of this salt is similar to that of $CaCl_2$ excepting *i*-amyl alcohols, which remains constant in the vapor phase over the whole range of concentrations of the salt in the wine, owing to the salt's poor solvating power.

Conclusions

When the salts are dissolved in aqueous medium, such as wine, they break up into ionics species which undergo solvation, resulting in the restructuring of the water (9). The practical effect is the removal of water from the medium, as a result of which the effective concentration of the other components present in the liquid phase increases, and consequently their concentration alters in the vapor phase in equilibrium. It is clear that the presence of the salts in the wine causes the wine's volatile components to move towards the vapor phase and enrich it.

Nevertheless, the removal of water from the medium also causes an increase in the solubility of some congeners (*i.e.*, *i*-amyl alcohols) which as a result are held more firmly in the liquid phase. It is the compromise between those two opposing effects which determines the behavior of these components and consequently whether their concentration increases or decreases in the vapor phase.

The concentration of ethanol in the vapor phase evolves according to a logarithmic expression with the concentration of the salt dissolved in the wine in equilibrium with the vapor. This function depends on the type of salt dissolved, so that what is called the efficiency factor of the salts varies in the order $CoCl_2 > CaCl_2 \simeq CuCl_2 > NaCl$.

Worthy of note is the catalytic action of $CuCl_2$, which causes a fall in the presence of acetaldehyde in the vapor phase with a corresponding rise in methyl and ethyl acetates. This effect is very important from the standpoint of industrial use of ethanol.

Finally, it should be stressed that all the foregoing took place in an equilibrium still (*i.e.*, single-stage) from which we may suppose that the effect of the salt will be much greater in industrial columns with their multiple contact stages, the separation much greater, and the consequent energy saving considerable.

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