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Water and Ethanol

1.1 Introduction

From a macroscopic perspective, wine is a mildly acidic hydroethanolic solution. As shown in Table 1.1, water and ethanol represent ~97% w/w of dry table wines. Ethanol is the major bioactive compound in wine and its presence renders wine and other alcoholic beverages inhospitable to microbial pathogens. Understanding the physiochemical properties of wine will first require a review of the basic properties of water and water–ethanol mixtures. More thorough discussions of the unique properties of water, including those specific to the food chemistry, can be found elsewhere [1].

1.2 Chemical and physical properties of water

Water is a hydride of oxygen, but has unique properties compared to other hydrides of elements nearby on the periodic table, as shown in Table 1.2. For example, the boiling point of water (100 °C) is far above that of hydrides of adjacent elements on the periodic table: HF (19.5 °C), H₂S (–60 °C), and NH₃ (–33 °C). Thus, water exists as a liquid at room temperature, while the other hydrides exist as gases. Similarly, water also has a higher heat of vaporization, heat capacity, and freezing point than would be expected as compared to nearby hydrides.

The unique properties of water are largely due to its ability to engage in intermolecular hydrogen (H) bonding, which results in stronger molecule-to-molecule interactions than in related compounds.

- Oxygen is more electronegative than hydrogen and an O–H bond is more polarized than N–H or S–H.
- The geometry and symmetry of an H₂O molecule allows for four concurrent H bonds per water molecule.

The ability of water to form strong H-bonds explains not only its higher boiling point than homologous hydrides, but also its high *surface tension*. A surface refers to the area in which two phases come into contact (e.g., water–air, water–oil, water–glass), and surface tension refers to the force needed to create an additional surface area between two phases, that is, to spread a water droplet on to a piece of wax paper.

Table 1.1 Composition of a typical dry table wine

Compound(s)	Concentration (% w/w)	Major roles in wine
Water	85–89	Tactile (mouthfeel) Major matrix component
Ethanol	9–13%	Tactile (pungency/heat, mouthfeel) Taste (astringency, bitter, sweet) Major matrix component
Glycerol	0.5–1.5%	Negligible, slight contribution to sweetness and body
Acids	0.6–1.0%	Taste (sour), pH buffering
Sugars	0.1–0.5%	Taste (sweet); minor effect on mouthfeel
Polyphenols	0.1–0.2% (red) 0.02–0.05% (white)	Color, mouthfeel (astringency)
Polysaccharides	0.05–0.1%	Mouthfeel
Minerals	0.05–0.2%	pH buffering; minor taste effects
Most odorants	<0.001%	Aroma

Table 1.2 Physical properties of water, ethanol, and their mixture (10% w/w ethanol in water)

Property	Water	Ethanol	10% w/w EtOH
Boiling point (°C) at 100 kPa	100	78	90.85
Density at 20 °C (g/mL)	0.998	0.789	0.983
Surface tension (mN/m)	73	22	48
Viscosity at 20 °C (Pa·s) × 1000	1.00	1.14	1.31

Compounds that are polar (or that contain polar functional groups) and are also capable of H-bonding are referred to as *hydrophilic* and tend to be more soluble in water, which in wine would include most sugars and ions like K^+ and SO_4^{2-} . Many compounds of importance to wine flavor, especially odorants, are *hydrophobic* and are characterized by the presence of hydrocarbon groups that are incapable of H-bonding. A snapshot at the molecular level would show water molecules preferably forming H-bonds with each other while interacting minimally with the hydrophobic solute. This imposes order upon the system, and dissolution of hydrophobic compounds in water tends to be entropically unfavorable. Colloquially, the preference of polar solvents to solvate polar compounds rather than non-polar compounds (and vice versa) is referred to as “like dissolves like.”

1.3 Properties of ethanol and ethanol–water mixtures

Water and ethanol are completely miscible: that is, they will mix with each other freely at any proportion. The mixing of ethanol and water will have profound effects on the structure of water because ethanol is *amphiphilic* – it has both a hydrophilic alcohol group (–OH) and a hydrophobic hydrocarbon chain (–CH₂CH₃). At concentrations <17% v/v, typical for most table wines, ethanol molecules are molecularly dispersed. The –OH group can participate in H-bonding in place of an H₂O molecule, while the –CH₂CH₃ group will interact minimally with H₂O. The addition of small amounts of ethanol to water will have several effects on the properties of the matrix:

- Decrease in boiling point. Because it is less capable of H-bonding, ethanol (78 °C) has a lower boiling point than water (100 °C, Table 1.2). Mixtures of ethanol and water have boiling points intermediary to

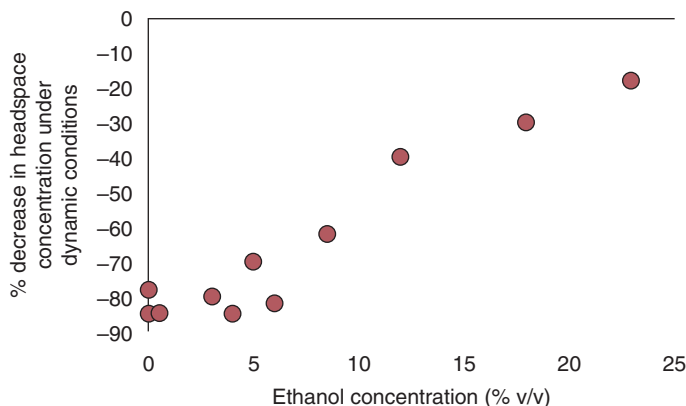


Figure 1.1 Decrease in ethyl butyrate headspace concentration under dynamic conditions (continuous sparging of the headspace by an inert gas). The smaller decrease observed at higher ethanol concentrations is a result of lower surface tension and faster replenishment of headspace volatiles. Data from Reference [3].

the pure compounds and show a negative deviation from Raoult's Law (Chapter 26.4). The effect of ethanol on boiling point is exploited in the analytical technique of *ebulliometry*, which uses measurements of the wine boiling point to calculate ethanol concentration [2].

- Decrease in surface tension. Because ethanol is amphiphilic, it will behave like a 'surfactant' – that is, in aqueous solutions it will preferably be found at interfacial surfaces, resulting in a decrease in surface tension (Table 1.2). At the molecular level, the hydrocarbon tail of ethanol will orient itself towards the non-aqueous phase (air, oil, etc.). One consequence of ethanol being both a surfactant and more volatile than water is that wine and other alcoholic beverages will form “tears” or “legs” along the sides of a glass.¹ A second consequence of greater importance to wine sensory properties is that as ethanol migrates to the surface it will bring with it other non-polar volatile compounds. These compounds can then volatilize, resulting in faster equilibration of aroma compounds between headspace and liquid (Figure 1.1 [3]). A practical consequence is that even though the concentration of volatiles in the headspace above water will be higher than over wine under static conditions, this concentration can decrease considerably under dynamic conditions, for example, if a glass is repeatedly sniffed. In contrast, the volatile composition of wine headspace will stay relatively constant.
- Decrease in matrix polarity. Mixing of ethanol and water results in a disruption of water structure and H-bonding. Thus, there will be a decreased entropy loss when hydrophobic volatile compounds dissolve in wine-like solutions as compared to pure water. There may also be a larger increase in enthalpy due to hydrophobic interactions between the hydrocarbon chain of ethanol and the solute. As a result, less polar compounds like vanillin (“vanilla” aroma; Table 1.3) will have greater solubility in ethanol, while polar solutes like sodium chloride will have lower solubility in ethanol because they are less able to participate in H-bonding. The effects of ethanol on solubility will be reconsidered in later chapters, such as on the precipitation of potassium bitartrate (Chapters 4 and 26.1).

¹Wine tears are an example of the *Marangoni effect*, in which liquids move from areas of low surface tension to areas of high surface tension. Evaporation of ethanol from the surface of wine results in an area of higher surface tension, which will be compensated for by migration of ethanol-rich wine from the bulk liquid to the surface. Eventually, this will result in formation of a ring on the walls of the wine glass, which will fall due to gravity.

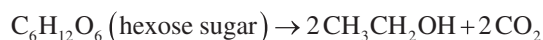
Table 1.3 Solubility of a non-polar (vanillin) and polar (sodium chloride) compound in water and in ethanol

Compound	Solubility in water at 25 °C	Solubility in ethanol at 25 °C
Vanillin	1.06 g/L	364 g/L
Sodium chloride	365 g/L	0.65 g/L

- Increase in viscosity. Ethanol is only slightly more viscous than water (1.14 versus 1.00 mPa·s at room temperature; Table 1.2). Addition of ethanol to water will result in an increase in viscosity greater than the individual components, from 1.31 mPa·s at 10% v/v up to a maximum of 2.9 mPa·s at 40% v/v.² Mixing ethanol and water will also result in a total volume less than the component volumes. For example, mixing of 50 mL of each solvent results in a final volume of 96 mL. These phenomena occur because addition of ethanol will disrupt the more open lattice structure of pure water.
- Formation of ethanol aggregates. The description of ethanol-in-water mixtures as molecular dispersions, e.g., ethanol molecules isolated from each other and completely surrounded by water molecules, is valid at concentrations up to 17% v/v. For solutions with 17–63% v/v ethanol, spectroscopic data indicates that ethanol begins to form molecular aggregates within the solution, as opposed to a true molecular dispersion [4]. These aggregates have been referred to as “micelle-like” and appear to have similar behavior to better known micelle-forming compounds like detergents. At concentrations >63%, water will form a molecular dispersion within ethanol.

1.4 Typical ethanol concentrations in wines

In alcoholic beverages, ethanol is formed by yeast via fermentation of hexose sugars (fructose, glucose). The Gay–Lussac equation describes this reaction:



In wines, these sugars are mostly derived from grapes, although sugars can also be legally added prior to fermentation in some regions (*chaptalization*). In principle, one mole of sugar should yield two moles of ethanol, but in practice this value is closer to 1.8 moles of ethanol. Alcoholic fermentation will be described in more detail in later (Chapter 22.1). Wine producers routinely measure ethanol concentrations to track fermentations, for quality control and for legal obligations.³ Most countries or wine regions place limits on minimum ethanol concentrations for a product to be called a wine, and a tax code may also be based on ethanol concentration.⁴

Unlike most compounds in wine, which are reported in units of w/v (g/L) or w/w (g/kg), it is common in both scientific and commercial settings to report ethanol concentrations in units of % v/v. A wine containing

²By comparison, the viscosities of olive oil and honey are usually about 80 and 5000 mPa·s, respectively.

³Regulatory documents usually refer to “alcohol” rather than “ethanol” because the former term is more widely understood. However, in this book we will preferably use the term ethanol because there are other alcohols in wine.

⁴From a legal perspective, ethanol is the only compound that is required to be in wine, since minimum and maximum ethanol concentrations for dry table wines are regulated in most countries. In the United States, CFR 24.7, a wine labeled “Table Wine” must have between 7 and 14% alcohol. Water is not explicitly required to be present, although it is not clear how one would produce a “water-free” wine!

12% v/v ethanol contains 120 mL of pure ethanol per 1000 mL of wine. Since the density of most wines is close to 1.0 g/mL at 20 °C, % v/v units can be converted to % w/v units by multiplying by the density of ethanol (0.789 g/mL at 20 °C). Thus, a 12% v/v wine with a density of 1.0 g/mL will have $(120 \text{ mL/L}) \times (0.789 \text{ g/mL}) = 94.7 \text{ g ethanol per L}$. A typical ethanol concentration encountered in dry wines is between 11 and 14% v/v. Because the amount of ethanol produced during fermentation is dependent on sugar concentration, wines from warmer regions with longer growing seasons tend to have higher ethanol concentrations than cooler regions. Red winegrapes are usually harvested later than white winegrapes, and as a result red wines typically have a higher ethanol concentration than whites. In recent years, there has been a tendency to pick grapes at higher sugar concentrations [5], such that average ethanol concentrations increased by 0.3–1.0% v/v across different wine regions between 1992 and 2007 [6].

1.5 Sensory effects of ethanol

The organoleptic effects that ethanol can have on wine flavor are diverse and are summarized in Table 1.4.

1.5.1 Major taste/tactile properties of ethanol

Ethanol appears to be a major factor determining bitterness in dry wines. For example, increasing the ethanol content from 8 to 14% results in over a 3-point increase in perceived bitterness on a 10-point scale [13]. By comparison, addition of catechin, a flavan-3-ol associated with bitterness (see Chapter 14) at concentrations well in excess of those found in wine (1500 mg/L) resulted in only a 1-point increase in bitterness. In a

Table 1.4 Summary of the sensory effects of ethanol in wine

Property	Comments
<i>Direct effects</i>	
Bitter taste	Commonly reported as major flavor property of ethanol in wine studies [7] Dominant sensation at 10% v/v ethanol [8]
Pungency (“heat”)	Commonly reported as major flavor property of ethanol in wine studies [7] Dominant sensation at 21% v/v ethanol [9] Perception due to activation of the TRPV1 receptor ⁵
Sweet taste	Dominant sensation at 4.2% v/v ethanol [9]
Ethereal-sweet smell	Can potentially have additive effects with other odorants
Perceived viscosity	Addition of ethanol to de-alcoholized wine results in maximum perceived viscosity at 10% v/v, but has negligible effects over the range of ethanol found in wines [10]
<i>Indirect effects</i>	
Astringency	Ethanol is reported to be astringent at high concentrations, due to denaturation and precipitation of salivary proteins. In real wines, ethanol results in a decrease in the intensity and duration of perceived astringency, possibly because ethanol disrupts interactions between proteins and tannins [11]
Taste	Ethanol can mask sourness [12]
Aroma	Ethanol can decrease the intensity of other odorants, either by masking or by decreasing their volatility [18]

⁵The TRPV1 channel is responsible for detection of damaging high temperatures, and also capsaicin in hot peppers.

separate study of 13 dry white wines with residual sugars < 10 g/L, differences in bitter intensity were best correlated with ethanol concentration (range = 10.8–14.4%), while no correlation was observed with bitterness and phenolics (range = 169–404 mg/L as gallic acid equivalents) [14].

Beyond bitterness, ethanolic solutions are also frequently described as “pungent” and “sweet” [12]. The dominant sensation will vary with concentration and among individuals, but generally seems to follow the pattern sweet → bitter → pungent with increasing concentration [8, 9]. Despite seeming contradictory, these descriptors can co-exist, e.g., a 10% v/v ethanol solution is reported to be better simulated by a combination of 3% sucrose and 0.005% quinine than either compound in isolation [8].⁶

1.5.2 Ethanol and wine odor

In isolation, ethanol is described as having a “fruity” or “ethereal, solvent-like” odor. Increasing ethanol concentration is usually reported to decrease the intensity and increase the threshold of odorants [15, 16]. For example, reconstitution studies using 7% in place of 10% ethanol resulted in a model wine with greater fruity and floral aromas, and the odor threshold of compounds in model wine are reported to be 10–100-fold higher than in water [15]. These behaviors could be explained by one of two effects:

- Masking. The presence of ethanol odor decreases the perceived intensity of other odors due to cognitive effects
- Matrix effect. Most odorants are hydrophobic and thus will be *more soluble* and *less volatile* in ethanol than in water, for reasons described earlier in this chapter. For example, the gas–liquid partition coefficients ($K_{g,l}$) of two common fermentation metabolites, isoamyl alcohol and ethyl hexanoate, decrease by almost a factor of 2 in a 10% v/v ethanol solution as compared to pure water (Figure 1.2) [17]. The effects of varying ethanol content over the range observed in table wines is more modest, with $K_{g,l}$ changing by less than 10% over an ethanol range of 5–17% v/v [18].

Sensory thresholds of odorants in 10% ethanol can be 10–100 times their threshold in pure water [15], far more than can be explained by the 2-fold decrease in volatility caused by matrix effects. Thus, the major

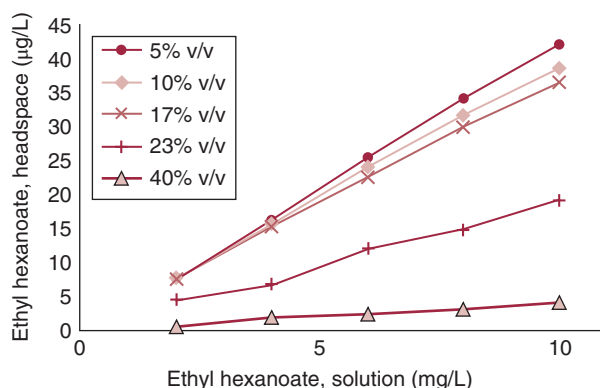


Figure 1.2 Effects of ethanol concentration (5–40% v/v) on ethyl hexanoate volatility. Data from Reference [18]

⁶Bitter and sweet taste receptors are structurally similar, and the property of artificial sweeteners having both bitter and sweet flavor is well known in the flavor industry (e.g., aspartame).

effect of ethanol on wine aroma is probably neurobiological (masking) rather than physiochemical (decreased volatility). However, in distilled spirits, it is possible that decreases in volatility could be of greater significance to sensory attributes. The flavor detection threshold of ethanol in water is reported to be 53 mg/L [19], but this number is not of particular relevance since all table wines will have concentrations well in excess of this value. Of greater importance is the *difference threshold*: that is, the minimum amount of ethanol that must be added to a wine before a sensorially detectable change can be demonstrated. Anecdotally, winemakers often report that differences as small as 0.1% v/v are detectable [20]. However, in formal sensory studies, differences of at least 1%, and sometimes as much as 4%, are necessary to cause detectable changes [21]. To understand this discrepancy it should be noted that many of the studies that have investigated the difference threshold for ethanol relied on addition of pure or near-pure ethanol to low-alcohol wines, which is not a common winemaking practice. In most wineries, differences in ethanol concentration are often realized by less selective approaches, such as allowing grapes to achieve higher initial sugar concentrations or removing ethanol after fermentation by spinning cone, reverse osmosis/distillation, or related techniques. These processes could result in other sensory changes to wine.

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10 *Part A: Wine Components and Their Reactions*

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