
Azeotropes from A to Z

Azeotropes seem to have become something of a hot topic of late. There was considerable discussion about them at the recent AIC Varnish Workshop held at the Getty Museum. I've been trying to make sense of them in the context of the Modular Cleaning Program (MCP) and solubility theory. In fact, a few years ago, I read that a new commercial paint stripper used a "patented azeotrope" formulation.

So, what is an azeotrope? Basically it is a mixture of solvents behaving badly. Well, not exactly badly, but unexpectedly. Understanding azeotropes, or at least being aware of their presence, can allow a better understanding of how certain solvent mixtures change as they evaporate.

The definition of an azeotrope (from American Heritage Dictionary) is: "A liquid mixture of two or more substances that retains the same composition in the vapor state as in the liquid state when distilled or partially evaporated under a certain pressure."

There are a few different types of azeotropes, but we will only discuss the boiling point minimum type – the one of interest to conservators. Given that restriction, the definition of an azeotrope can become simply: "A liquid mixture of two or more substances that has the lowest boiling point and that boiling point is also lower than any of the pure liquids from which the mixture was combined."

Boiling point and vapor pressure are inversely related. A higher vapor pressure creates a lower boiling point. (When the vapor pressure equals atmospheric pressure, the solvent is boiling.) Since the azeotrope has the lowest boiling point possible in a mixture, it has the highest vapor pressure. Therefore, the azeotrope evaporates out of a solution preferentially.

If the mixture is such that the bulk of the solution has the same composition as the azeotrope, the mixture evaporates just as if it were a single solvent, not changing composition as it evaporates. If, however, the bulk solution is mixed to any other proportion, the proportions of solvents in the mixture will change as the azeotrope evaporates away.

Not all solvent mixtures form azeotropes. Azeotropes tend to form between solvents with different solubility characteristics. The azeotrope arises due to an interaction between the solvents in the solution.

Let's consider a few examples. Acetone boils at 56.05°C, n-hexane at 68.73°C, and n-heptane at 98.35°C.

Heptane and hexane do not form an azeotrope. The hexane evaporates faster and the heptane slower, but both evaporate in proportion to their concentration in solution and their respective vapor pressures. This also means that a mixture of heptane and hexane can be separated by distillation.

However, a mixture of 54.4% acetone and 45.6% hexane boils at 49.8°C. That's 6° lower than the acetone alone and nearly 20° lower than the hexane.

If we mix acetone and n-heptane, the azeotrope consisting of 9% acetone and 91% heptane boils at 55.6°, slightly below acetone and more than 40° below heptane.

Forgetting for the moment that hexane is a toxicological minefield and no conservator should be using the stuff, how can the knowledge of the existence of the azeotrope between acetone and hexane be exploited?

If we wanted to have the fastest evaporating solvent possible based on these two quick evaporating solvents, it would be best to use a mixture of 54% acetone and 46% hexane. If we wanted the cleaning solution (or solvent for an adhesive) to become less polar as it dried, we would want to have the amount of acetone below 54%.

If we were to mix 20 ml of acetone with 80 ml hexane, something interesting would happen as the solvent mixture evaporated. Because it has a lower boiling point, the 54/46 acetone/hexane would evaporate first (bp 59.8°). The 20 ml of acetone would evaporate along with 16.8 ml of the hexane. This would leave 63.2 ml of nearly pure hexane behind, evaporating somewhat more slowly (bp 69°). So this mixture that appears to be 20% acetone/80% hexane, behaves like 36.8% acetone/hexane azeotrope and 63.2% hexane.

This could be exploited in, say, a solvent cleaning (remembering we don't really use hexane for health and safety reasons). Suppose a discolored resin layer is soluble in the mixture of acetone and hexane, but not affected by hexane alone. In this case, the solvent would get progressively "weaker" as the azeotrope evaporated taking the acetone out of the solution disproportionately with the hexane.

By the same token, this could be a real problem if we were basing a varnish or adhesive formulation on this solvent mixture. Assuming that the resin is soluble in acetone/hexane but not the hexane alone, we would run the risk of the resin precipitating out of solution as the acetone/hexane azeotrope evaporated away. By the time the solvent volume was down to half, the acetone would be gone and you would have your resin at twice its starting concentration, sitting unhappily in nearly pure hexane.

One problem we face in conservation is that we don't always use pure chemical solvents. Some solvents we consider pure are actually already azeotropic mixtures. The azeotrope for ethanol/water is 95% -- you simply can't remove the remaining water by conventional distillation.

The petroleum solvents we use are mixtures, the components of which can vary from manufacturer to manufacturer, from refinery to refinery, and from the crude oil feed stock that was processed in the refinery. All we know about their composition is their boiling range and aromatic content. This actually tells us a great deal about their solvent strength, but may lead us into uncharted waters when we consider solvent mixtures that could result in azeotropes being formed.

Let's, for a moment, pretend that there is a proprietary solvent that consists of a mixture of n-hexane and n-heptane. It has a wide boiling point range but is otherwise a moderately fast evaporating and well-behaved solvent.

Now we make a mixture of this solvent blend with acetone. The first component to evaporate out of the solvent would be the acetone/hexane azeotrope (bp 49.7°). Once either of the components of the azeotrope is depleted, the next lowest boiling point component would be either the hexane (45.6°), if it hadn't been depleted when the azeotrope evaporated away, or the acetone/heptane azeotrope (bp 55.8°). If there were still acetone present, it would be the last component to evaporate away (56.1°) because all the heptane and hexane would have been consumed in the evaporation of the azeotropes. The other possibility is that the heptane would be the last component after azeotropic evaporation removed both the hexane and acetone.

This is a really complicated scenario. One can imagine this and even more complicated evaporation patterns occurring when petroleum distillates with multiple components are mixed with polar solvents. Plus, there is always the presence of water in the polar solvent which can add additional azeotropes.

Let's compare hexane and heptane. They are very similar solvents. Each is a straight-chain hydrocarbon – hexane with six carbons and heptane with seven. Except for the difference in their boiling points, they behave very similarly. (And that is why I encourage everyone to use heptane instead of hexane. That's because toxicologically speaking, they behave very differently in the liver – hexane is reduced into a really nasty intermediate and heptane is not.)

But when we look for a pattern in their azeotrope formation, it is hard to see any rhyme or reason behind the numbers. When we look at mole fractions (that's the molecule to molecule ratio rather than volume percentages) we see that acetone/hexane has a molar ratio of .68/.32 while the acetone/heptane molar ratio is .17/.83. Odder still, if we look at the azeotropes of hexane and heptane with n-butanol, we find the molar ratio for n-butanol/hexane is .04/.96 while the ratio for n-butanol/heptane is .23/.77 – the absolute opposite trend we saw with the acetone azeotrope.

There are higher order azeotropes – ternary and quaternary – but they are less common and more difficult to characterize. Perhaps the most famous is the water/ethanol/benzene azeotrope (bp 64.9°), which has a lower boiling point than even the water/ethanol azeotrope (78.2°C). So one trick to making 100% ethanol (anhydrous or absolute ethanol) is to add a bit of benzene (the carcinogenic one) to the 95% ethanol/water mixture. Now the benzene/water/ethanol azeotrope evaporates away first. Excess benzene must be added to make sure that all of the water is boiled away in the azeotrope. After the water is gone, the benzene/ethanol azeotrope is distilled off at 67.8°, leaving just pure ethanol behind (bp 78.2°). [There are a number of other ways to produce absolute ethanol. However, if the benzene

azeotrope distillation process was used, there will be traces of benzene in the alcohol. That's why smart chemists know to stay away from the lab punch made with absolute alcohol.]

Interaction with the Solute or Substrate

Solvents can also interact with the solute (be it resin in a varnish or adhesive) or a substrate (perhaps a paint film we are working very hard not to dissolve). The solute or substrate may sequester a component of the solvent solution, releasing it very slowly over a prolonged drying. This does not appear to alter the azeotrope except that that sequestered solvent is not available to participate in azeotrope formation.

There has been considerable discussion about the use of small amounts of slow evaporating, high polarity solvents as components in varnishes and cleaning solutions. The concerns are that the slow evaporating solvent would be the last component to leave the paint surface and therefore exert a solvent effect disproportionate to its concentration in the original solution. Many conservators are recommending against this practice.

This might not be as much of a concern if the slow evaporating solvent formed an azeotrope with one of the other solvents in the solution, as is the case for n-butanol mixtures with hexane, heptane, and octane. Unfortunately I have found no literature on the azeotropes of benzyl alcohol. I would expect it to form similar azeotropes with the components of aliphatic hydrocarbons, but azeotropes often do not behave as expected.

Whether or not these slow evaporating, high polarity solvents form an azeotrope and do, in fact, leave the painting's surface before the other component, the solvent will still have the opportunity to adsorb onto the paint surface and be sequestered from participating in azeotropic evaporation. But this amount or residual adsorbed solvent would be much, much less than the puddle of solvent we might expect to find if azeotropes were not involved.

Azeotropes and Solubility Theory

An azeotropic mixture of solvents will have an anomalous solubility parameter as well as a reduced boiling point and an increased vapor pressure. This makes sense as solubility theory is based on the thermodynamic energy needed to separate solvent molecules (which in turn is related to boiling point and vapor pressure). An azeotrope should be treated as a single new solvent with its own solubility parameters.

The Hildebrand solubility parameter, δ , is defined:

$$\Delta \delta^2 = \Delta H_V - RT/V_M,$$

which relates the solubility parameter to the molar enthalpy of vaporization (ΔH), the gas constant (R), the temperature (T , in °K) and the molar volume (V_M , molecular weight divided by density).

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The Hildebrand Scott Equation is an empirically derived estimate of the molar enthalpy of vaporization based only on the boiling point, T_b , of the solvent:

$$\Delta H = -12340 + 99.2(T_b) + 0.084(T_b)^2$$

Unfortunately, since we don't know the density of the azeotropic mixture, we can't calculate the Hildebrand solubility parameter for comparison with the extrapolated value.

By the Numbers

Azeotrope data is usually published in a scientifically succinct but very confusing way. Here is a sample of the data on acetone/hexane and acetone/heptane azeotropes:

	Boiling pt.°C	Mole fraction	Azeotrope Boiling pt.°C
acetone	56.05		
hexane	68.73	.681	49.8
heptane	98.5	.91	55.85

The first line lists one component of the azeotrope and its pure boiling point. Each of the solvents indented below form an azeotrope with the solvent in the first line. The boiling point of each pure secondary solvent is listed. The Mole Fraction column lists the mole fraction of the first component in the listing (acetone). And, finally, the boiling point of the azeotrope is listed.

To make these numbers useful to the conservator, we need to convert the information into volume percentages. To do this, we also need to know the molecular weight and density (specific gravity) of each component.

Chemical	Molecular Weight (g/mole)	Density (g/ml)
acetone	58.081	0.7899
n-hexane	86.179	0.6548
n-heptane	100.206	0.6837

Looking at the first entry in the azeotrope table, we see that acetone forms an azeotrope with hexane with a boiling point of 49.8 and at .681 mole fraction acetone (and therefore .319 mole fraction hexane).

To convert mole fraction to weight, we multiply each mole fraction by the solvent's molecular weight: acetone $.681 \times 58.081 = 39.55$; hexane $.319 \times 86.179 = 27.49$. (This works out to 59% acetone to 41% hexane by weight.)

To convert weight to volume, we divide by the density: acetone $39.55 / 0.7899 = 50.07$; hexane $27.491 / 0.6548 = 41.98$.

To convert to percentage, add both volumes (92.05) and divide each by that total volume: acetone $50.07 / 92.05 = 0.544$ or 54.4%; hexane $41.98 / 92.05 = 0.456$ or 45.6% by volume. (Just as advertised above.)

Other times the percentages of each solvent is given. One reference I used (an earlier version of the CRC Handbook) does not specify whether the percentages are by volume or weight. Based on comparing the values calculated from mole fraction data from another source, the tabulation seems to be by weight percent, but I'll never know for certain. Because these are measured values, different measurements by different people can give differing azeotrope concentrations.

There is an additional bit of information you might need to filter through when looking up information on azeotropes. We have been looking at azeotrope values at standard pressure. Often the data includes the information listed above but tabulated at various pressures. Azeotropes can appear and disappear at different pressures. In fact, ethanol can be distilled to greater than 95% using vacuum distillation because the azeotrope simply does not form at reduced pressure.

What Does It All Mean?

Of what use are azeotropes? Honestly, I'm not entirely sure. In my mind, I like to know when they exist and that an azeotrope might have an effect in a treatment (for better or worse). When I find a combination of solvents that solve a problem (and I'm in a virtuous mood), I will look to see if there is an azeotrope for those solvents with similar proportions to what I'm using. If appropriate I might consider reformulating the solution (and re-testing it) at the azeotrope.

Because so many of the solvents we commonly use are mixtures of indeterminate composition, it is even more difficult to know if and how an azeotrope might affect the behavior of a cleaning system or solvent mixture for a varnish or adhesive.

Lastly, you also may see reference to a zeotrope. A zeotrope is simply a solvent mixture that does not form an azeotrope at a given pressure. [I just added that so I could live up to the title of this article and end with a "Z"].

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Azeotropic Data							
Component 1	Component 2	Temperature (°C)	Composition (wt %)	Component 1	Component 2	Temperature (°C)	Composition (wt %)
acetone	n-heptane	9.2	56.05	ethanol	water	96.5	78.5
			55.85			3.5	100
acetone	n-hexane	54.4	56.05	ethanol	xylene	86.1	78.5
			49.7			13.9	139.12
acetone	water	99	56.05	n-heptane	isopropanol	53.9	98.5
			54.40			46.1	82.3
benzyl alcohol	water	8.6	205.31	n-heptane	methanol	52.2	98.5
			99.9			47.8	64.6
n-butanol	n-heptane	15.6	117.73	n-heptane	water	90.8	98.5
			93.3			9.2	100
n-butanol	n-hexane	2.4	117.73	n-hexane	isopropanol	81	68.73
			67.0			19	82.3
n-butanol	toluene	28.4	117.73	n-hexane	methyl ethyl ketone	75.7	68.73
			105.6			24.3	79.59
n-butanol	water	64.1	117.73	n-hexane	n-propanol	96.7	68.73
			93.0			3.3	97.2
n-butanol	xylene	76.2	117.73	n-hexane	water	96.3	68.73
			116.8			3.7	100
dimethylformamide	n-heptane	4.4	153	isopropanol	methyl ethyl ketone	30.5	82.3
			97			69.5	79.59
ethanol	ethyl acetate	33.9	78.5	isopropanol	methyl ethyl ketone	1	82.3
			71.8			89.9	79.59
ethanol	ethyl acetate	9.6	78.5	water		9.1	100
			70.2	isopropanol	toluene	60.4	82.3
ethanol	water	82.4	77.11			39.6	110.63
			70.2	isopropanol	toluene	41.2	82.3
ethanol	n-heptane	44.4	78.5			47.6	110.63
			72	water		11.1	100
ethanol	n-heptane	30.5	78.5	isopropanol	water	89.9	82.3
			68.8			10.1	100
ethanol	n-hexane	18.1	78.5	methanol	toluene	74.2	64.6
			58.7			25.8	110.63
ethanol	n-hexane	10.3	78.5	n-propanol	toluene	50.9	97.2
			56			49.1	110.63
ethanol	water	87.7	68.73	n-propanol	water	75.9	97.2
			56			24.1	100
ethanol	methyl ethyl ketone	34.5	78.5	n-propanol	xylene	94.4	97.2
			74.8			5.6	139.12
ethanol	methyl ethyl ketone	14.6	78.5	toluene	water	82	110.63
			73.2			18	100
ethanol	water	76.4	79.59	xylene	water	63.4	139.12
			73.2			36.6	100
ethanol	toluene	70	78.5				
			76.7				
ethanol	toluene	39.8	78.5				
			74.4				
ethanol	water	50	110.63				
			74.4				
ethanol	water	10.2	100				