Chemistry and Physics of Vanillin

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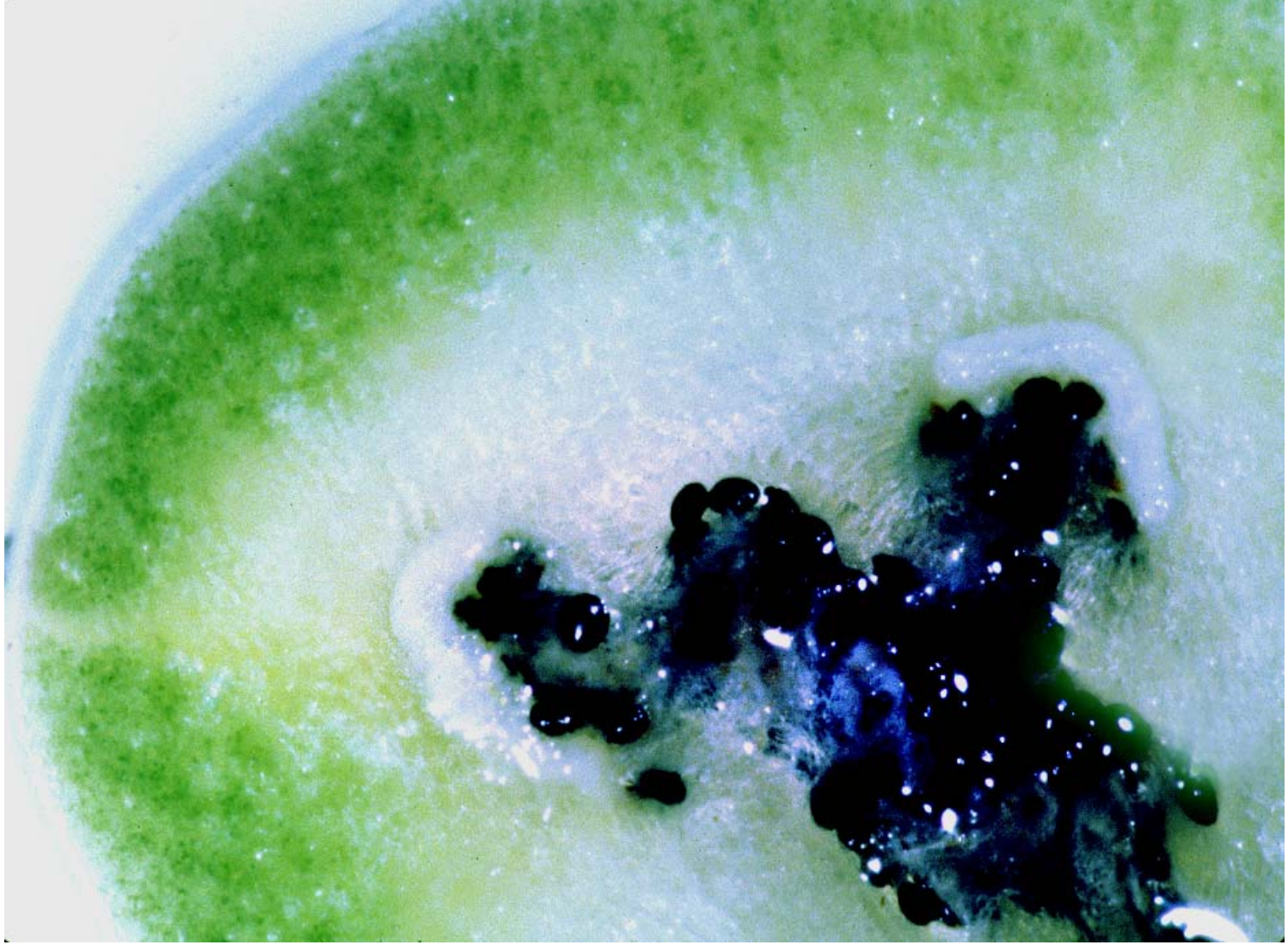
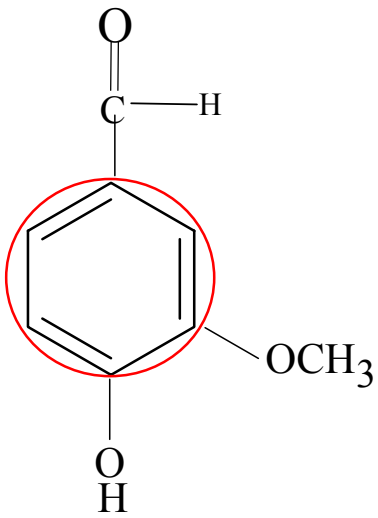
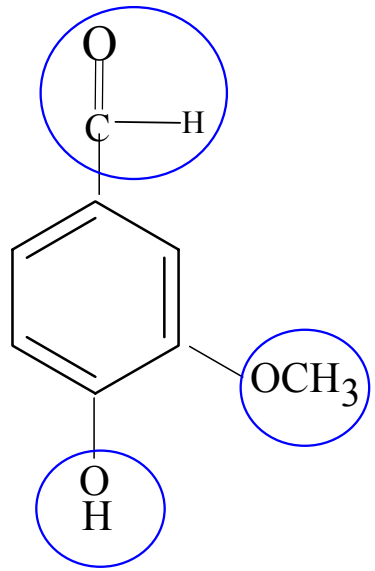
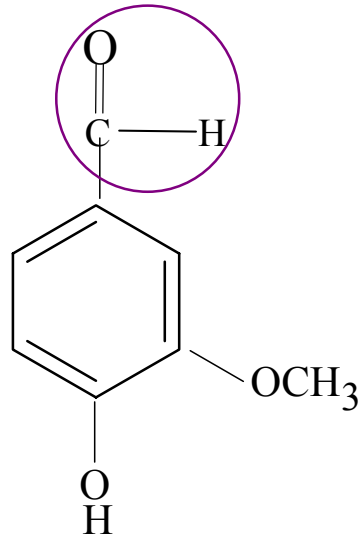


Cross section of vanilla bean showing a dark central cavity (seeds) surrounded by vanillin forming cells.





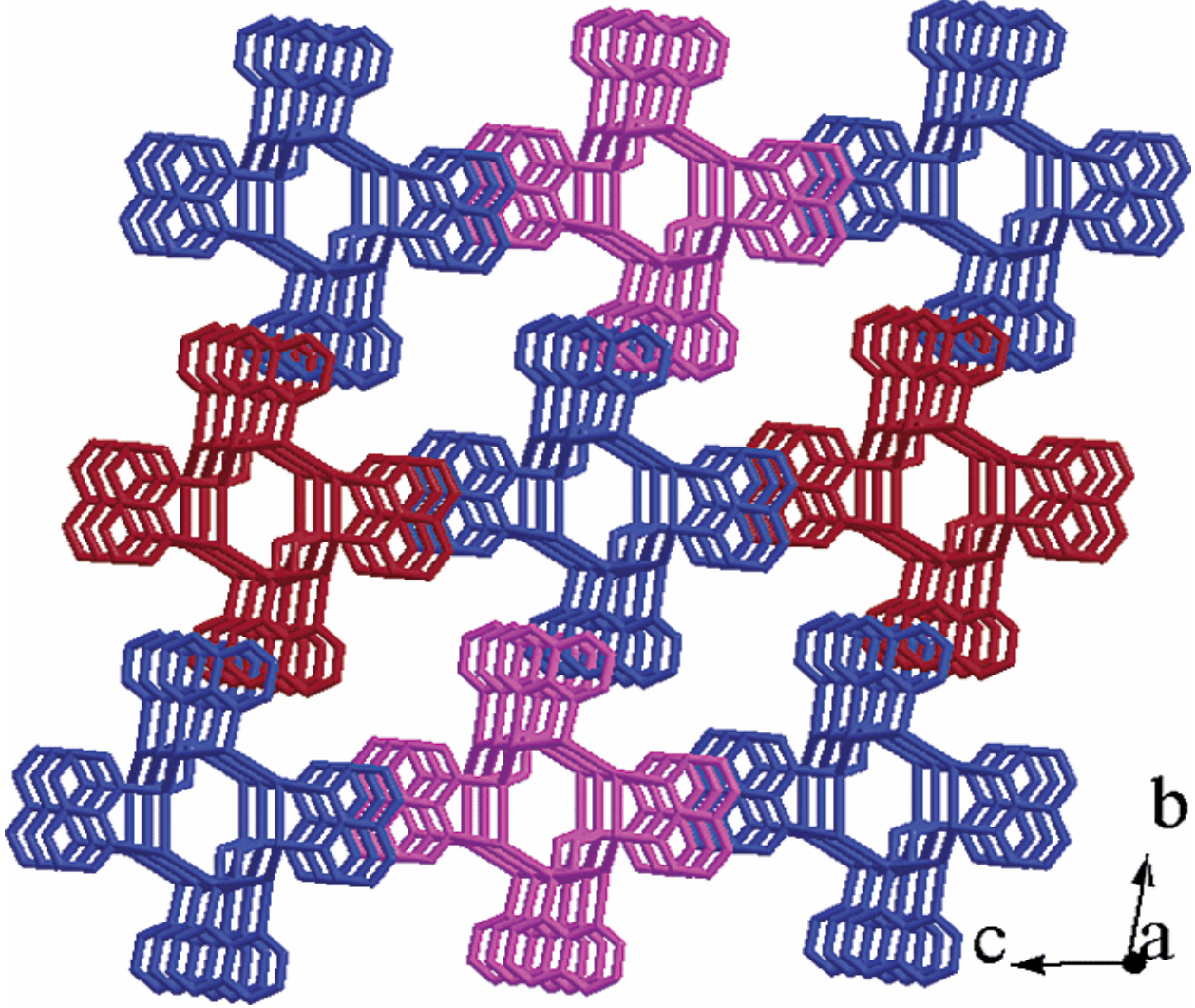


Hydrophobicity of the aromatic ring

Hydrogen bonds (intra and intermolecular)

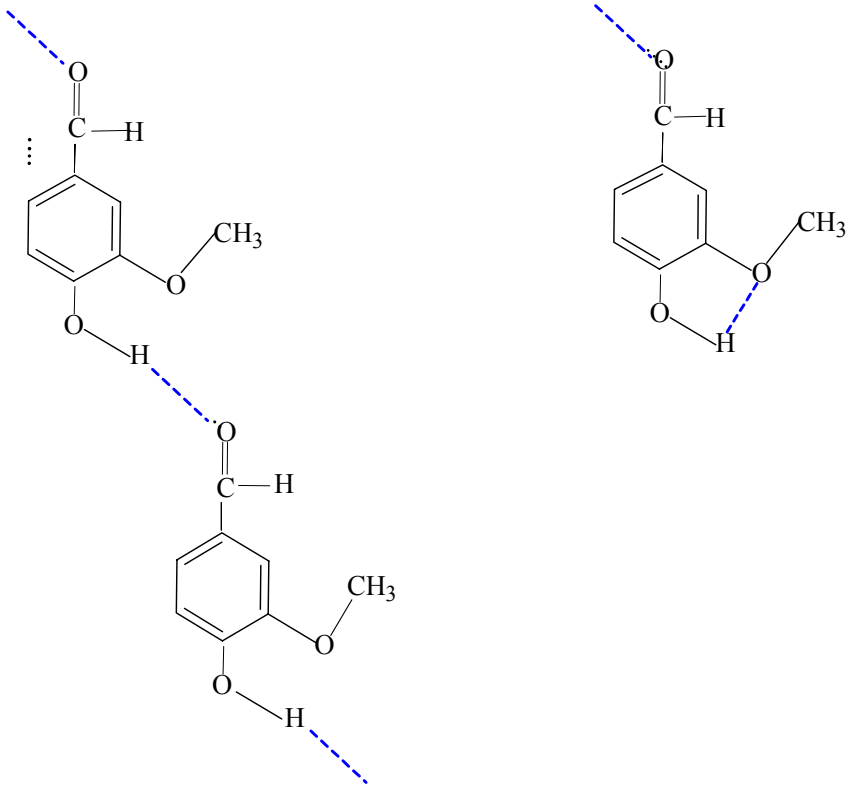
Reactivity of a carbonyl group (Maillard Reaction)

Molecular features of vanillin, including hydrophobicity, efficacy for forming hydrogen bonds and reactive carbonyl group, which could influence the fate of vanillin during various handling stages.

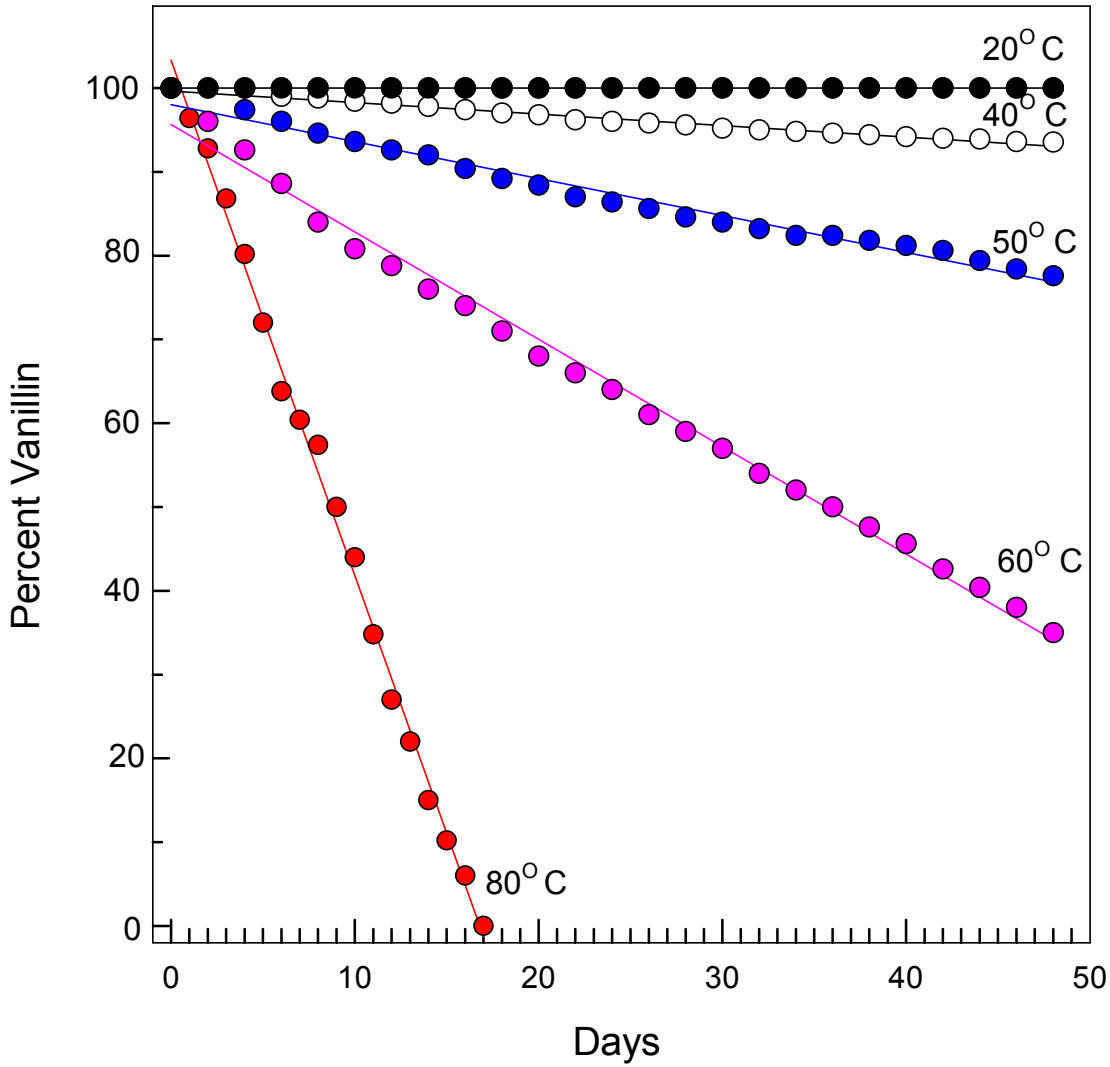


π- π stacking of aromatic rings. This phenomenon, stemming from the hydrophobicity of aromatic compounds contributes to the tendency of vanillin to form aggregates.

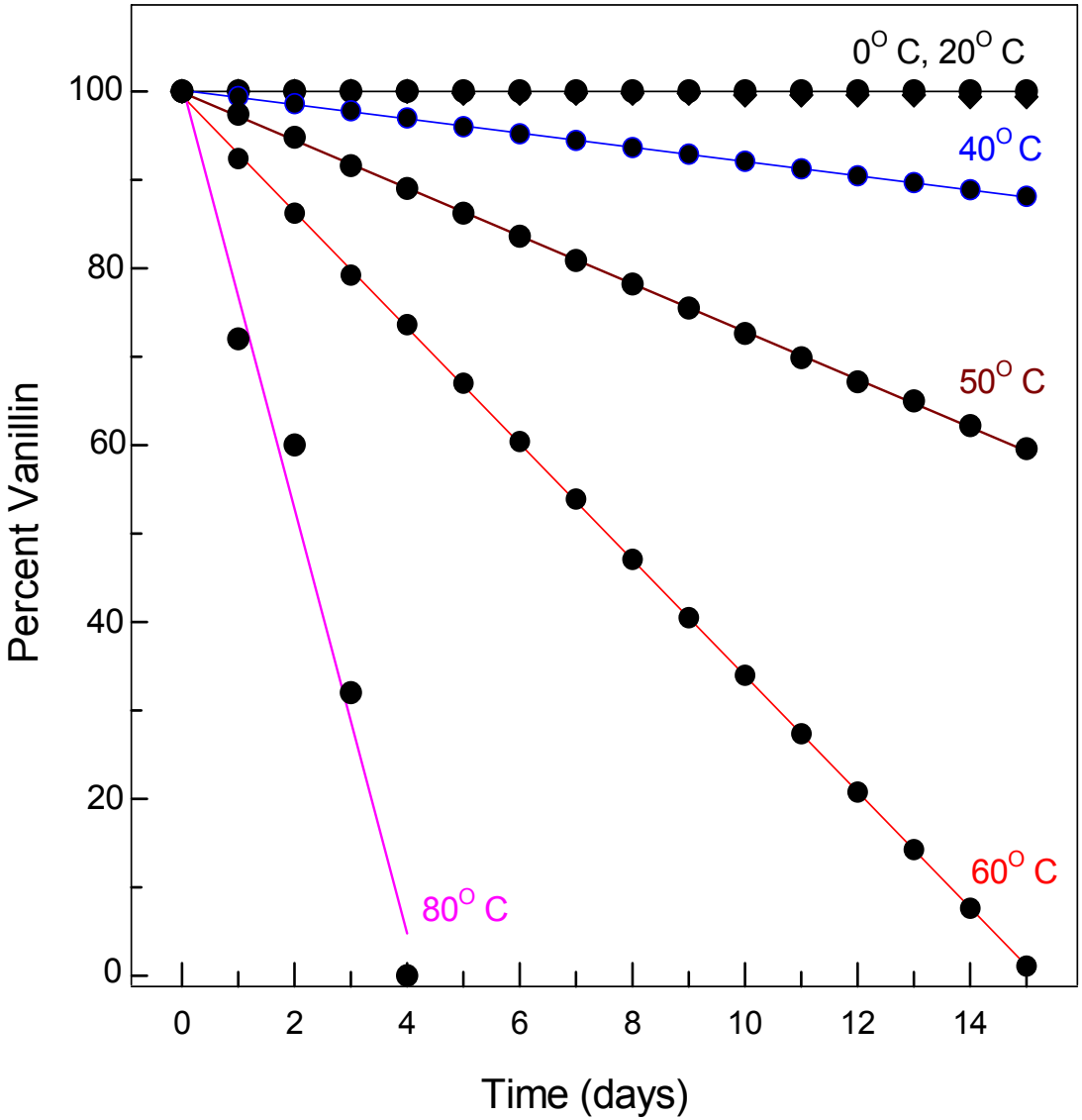
Inter and Intra Hydrogen Bonds in Crystalline Vanillin*



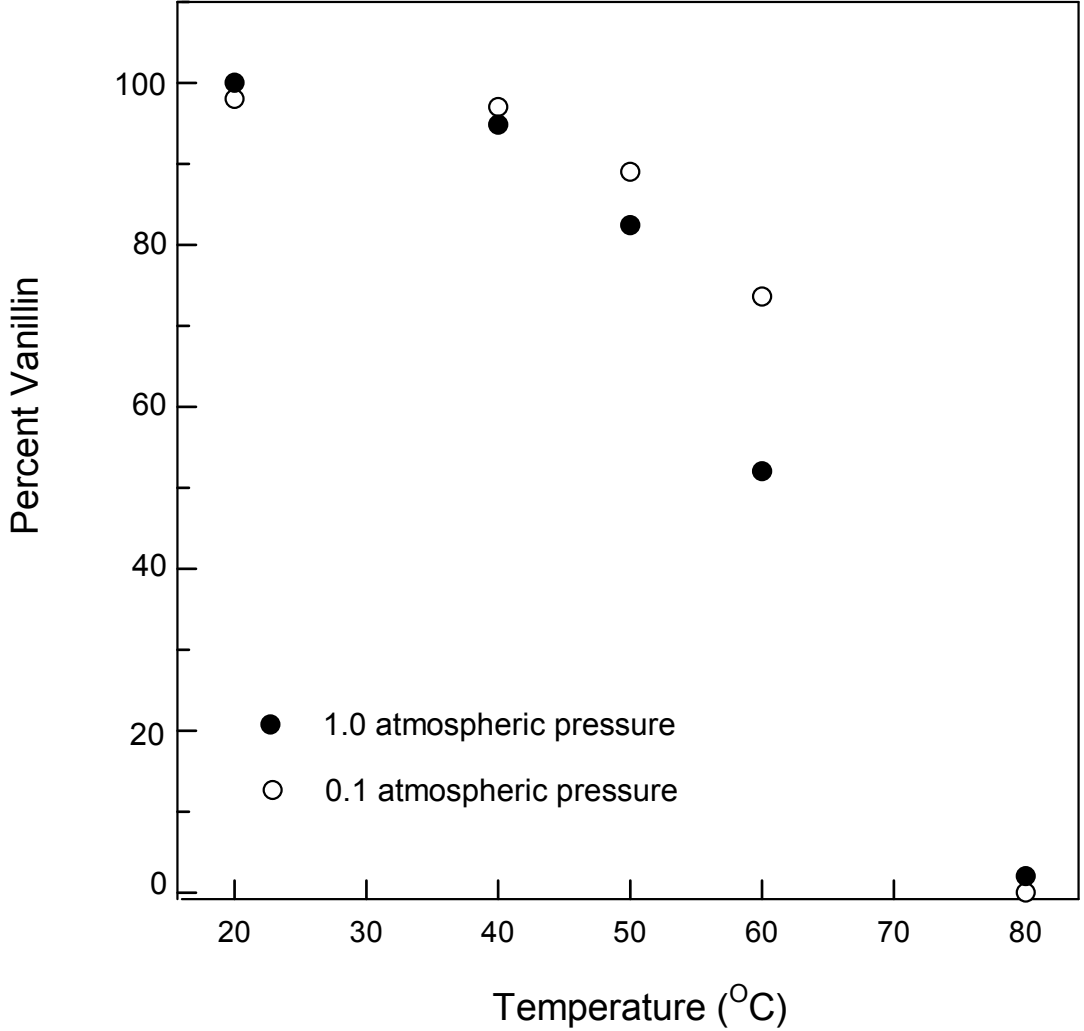
* Adapted from: Aihara A (1973) A study of hydrogen bonds in Vanillin I. Denki Tsaushin Daigaku 24:71-75



Rate of disappearance of dry vanillin held at atmospheric pressure and at different temperatures.

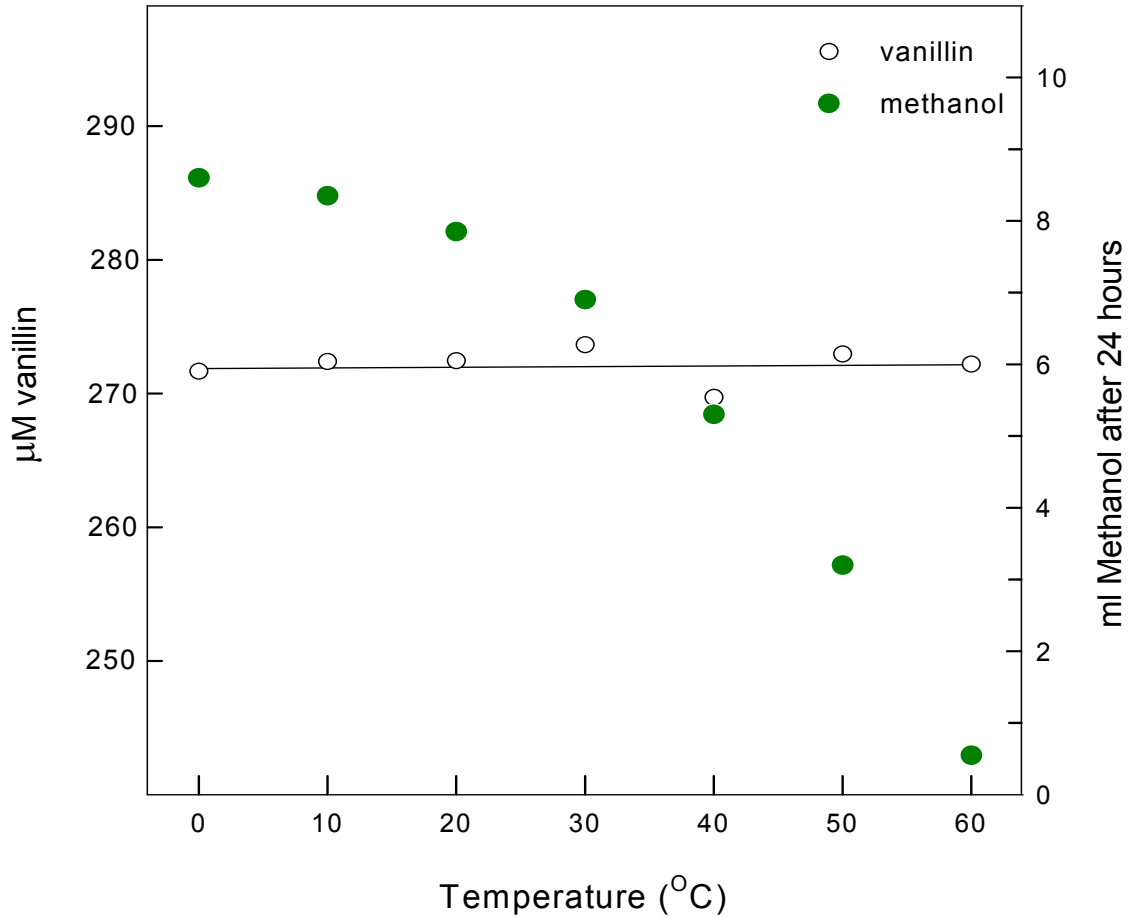


Rate of disappearance of dry vanillin held at 0.1 atmospheric pressure and at different temperatures.

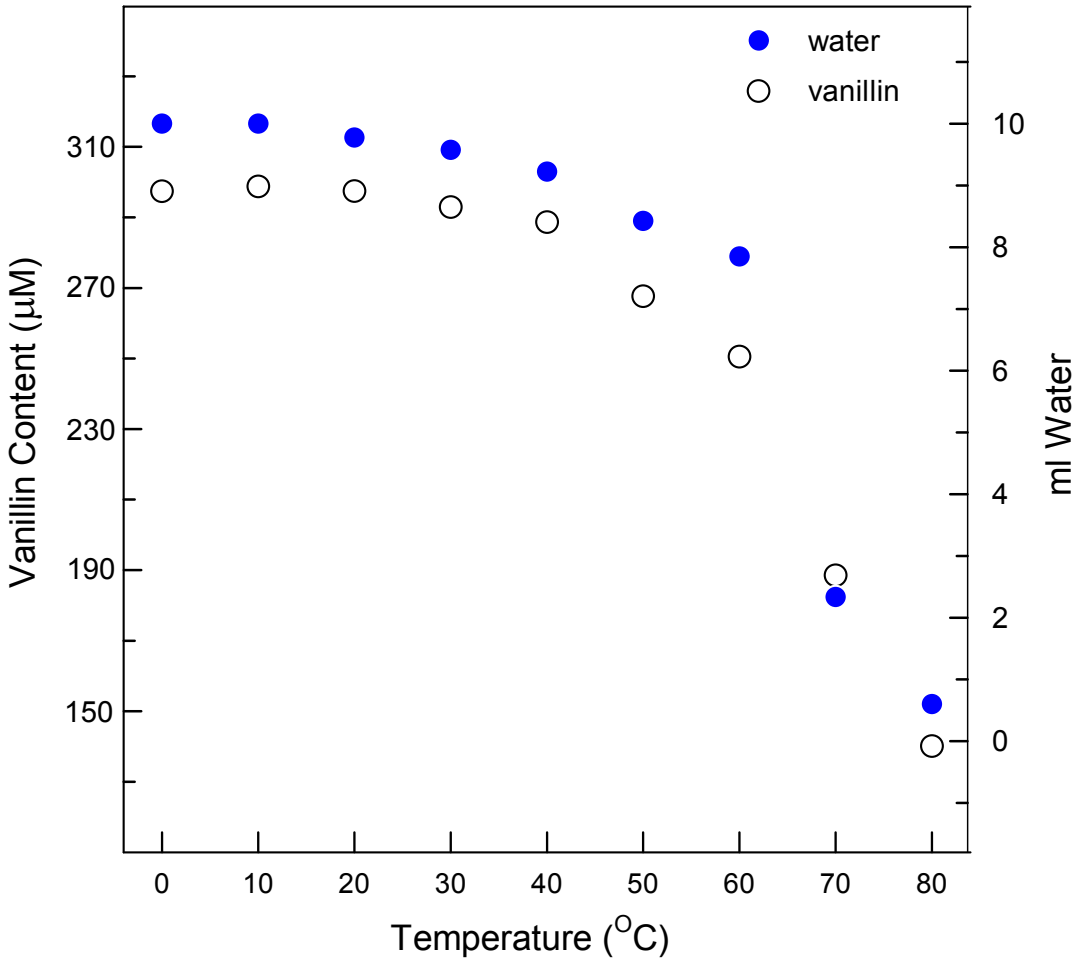


Disappearance of vanillin held at 1.0 or 0.1 atmospheric pressure.

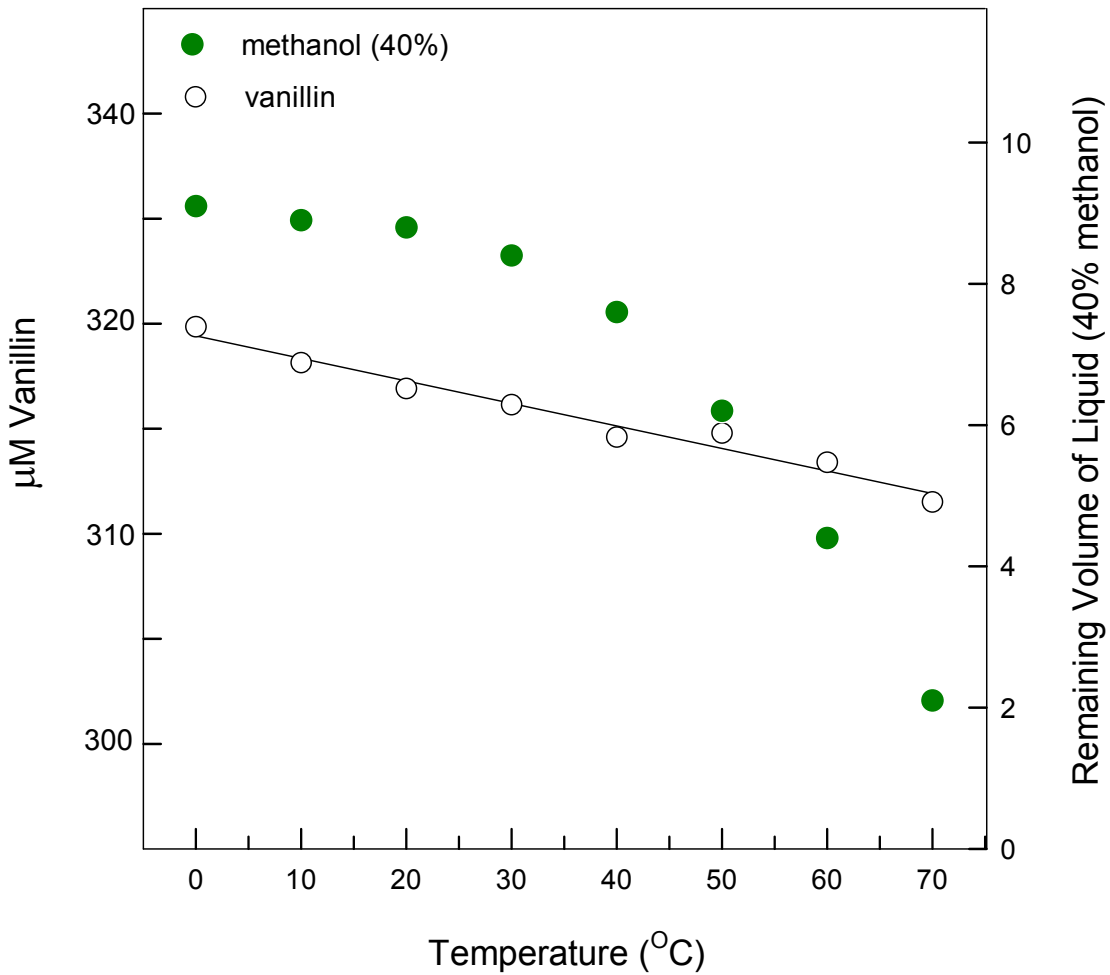
Vanillin was held for 18 and 4 days at 1.0 or 0.1 atmospheric pressure, respectively. The data shows that vanillin disappearance is greatly accelerated above 40° C.



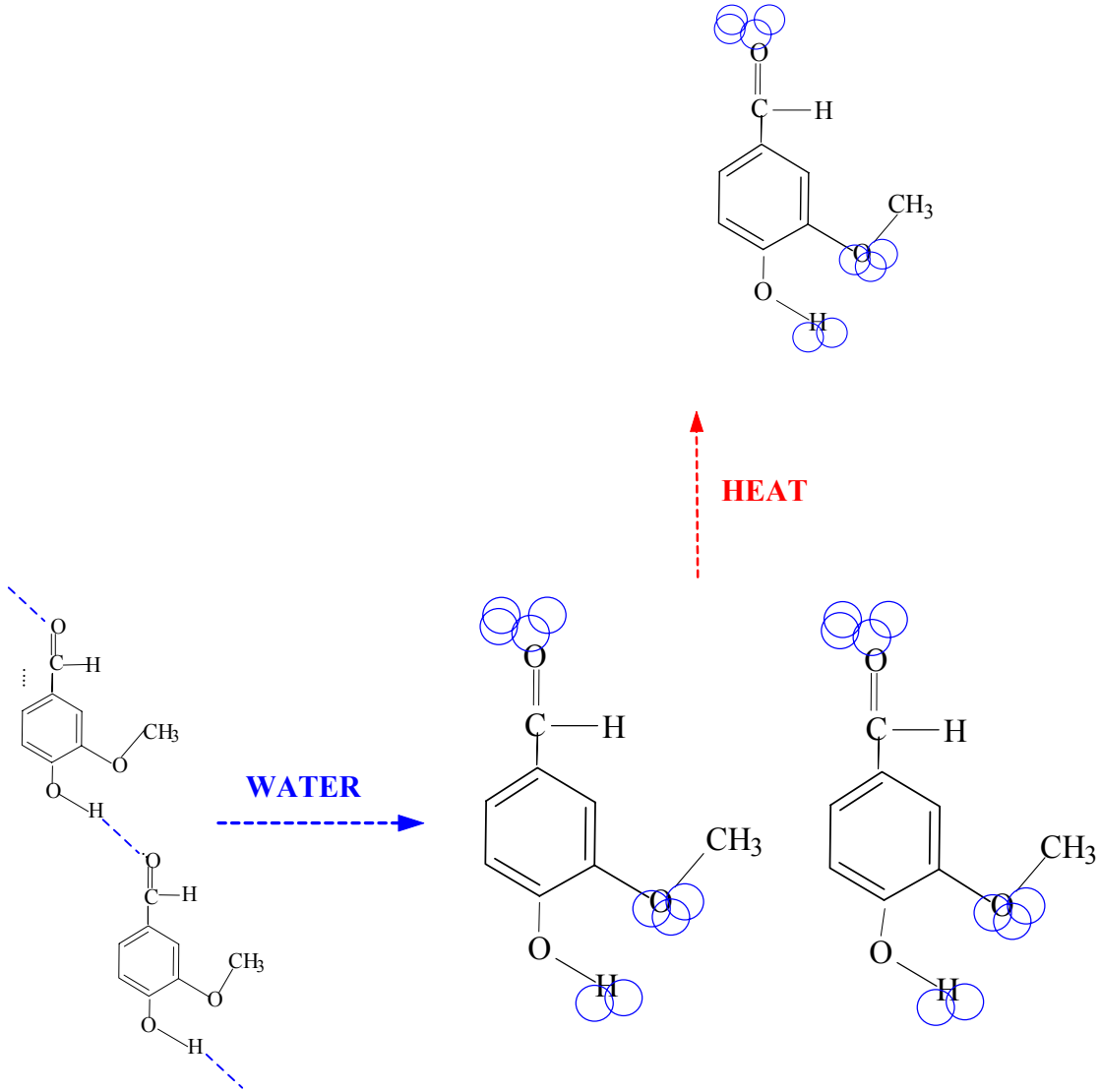
Vanillin content solubilized in 100% methanol and held for 24 hours at different temperatures. The data shows that while methanol is volatilized vanillin remains in solution.



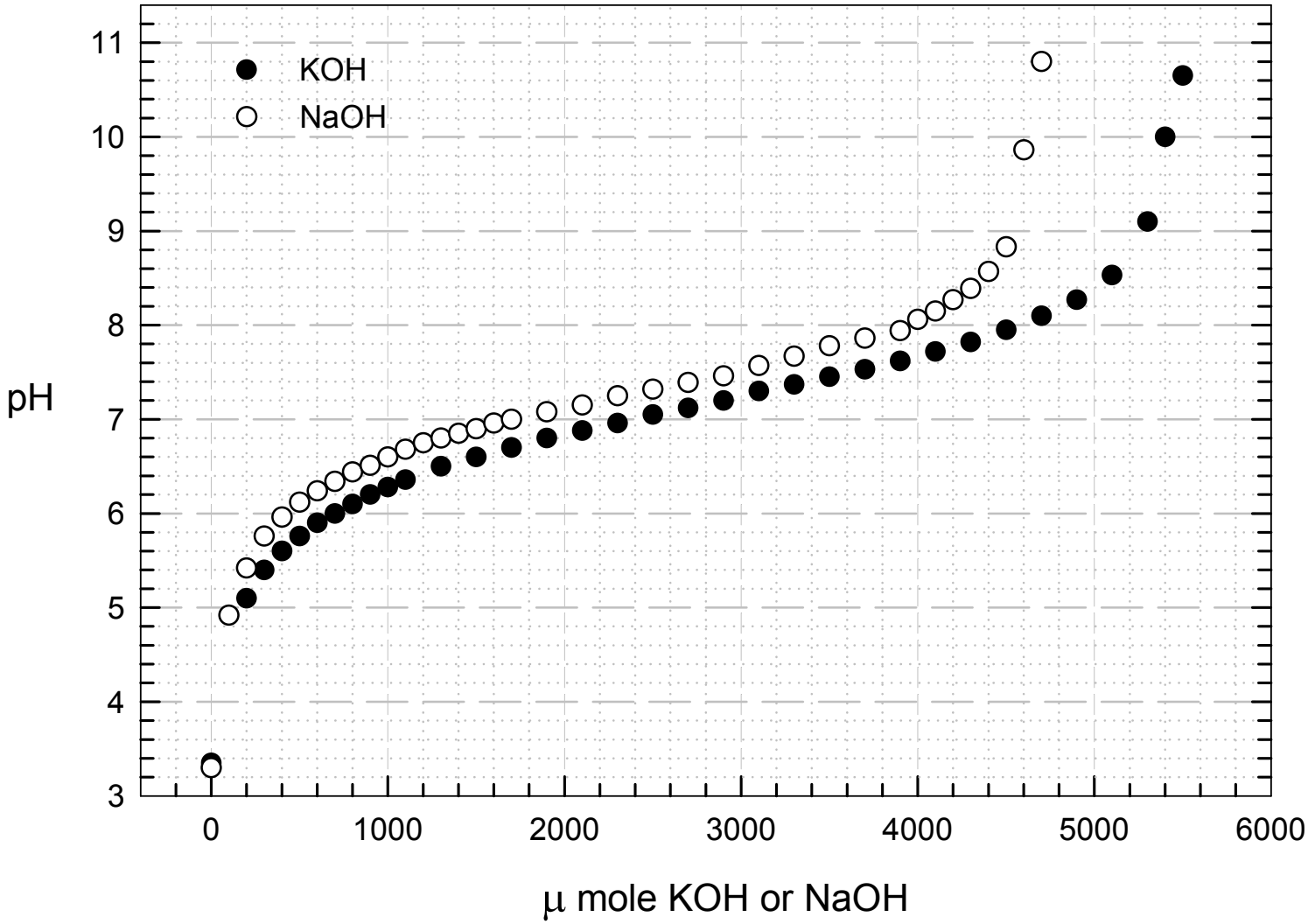
Vanillin content solubilized in water and held for 48 hours at different temperatures. The data shows That disappearance of vanillin is correlated to the rate of water disappearance.



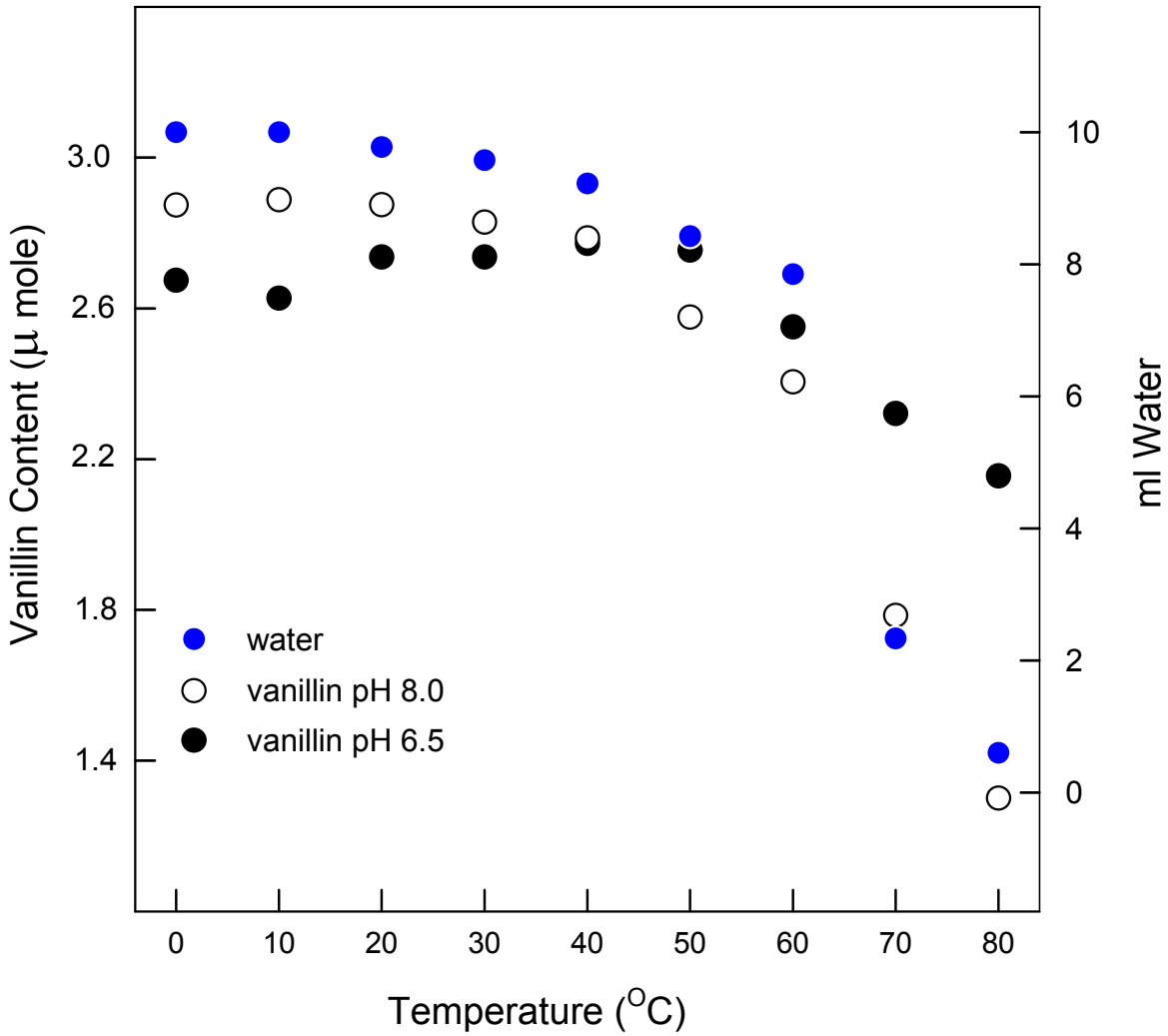
Vanillin content solubilized in 40% methanol-water solution and held for 2 days at different temperatures. The data shows that presence of water caused some disappearance of vanillin.



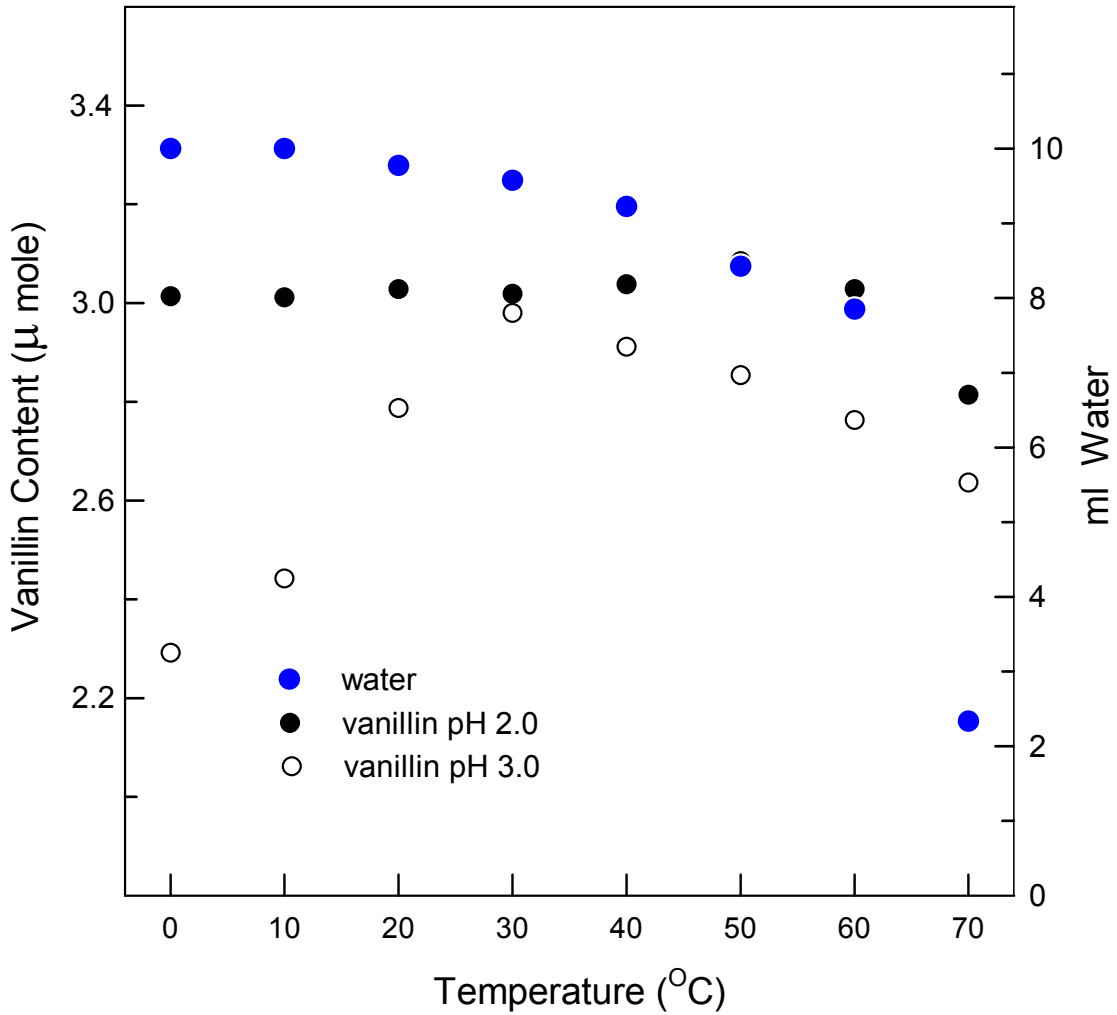
A hypothetical scheme indicating that hydration of vanillin, due to vanillin-water hydrogen bonding, leads to the volatilization of vanillin-water complex.



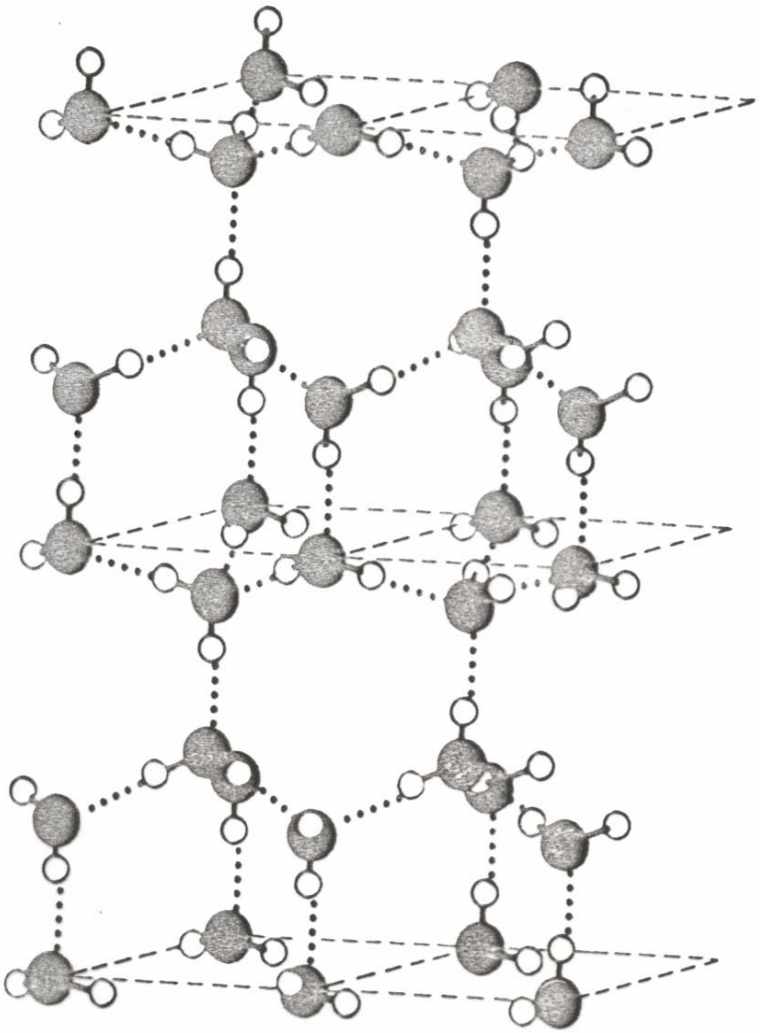
Titration curve of vanillin in water.
The data shows that native vanillin is acidic and, moreover, exhibits a substantial buffering capacity.



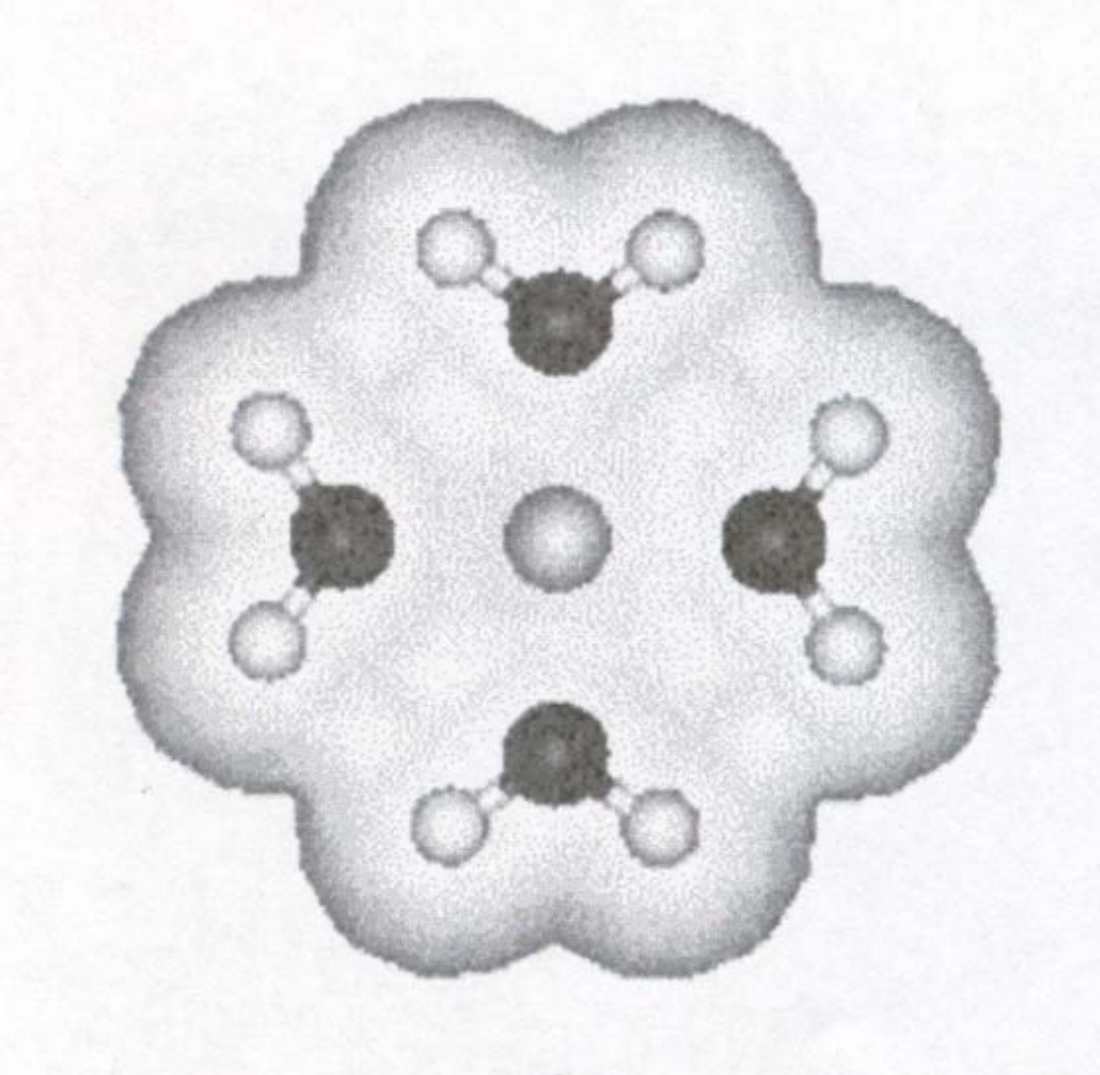
Vanillin content in water, adjusted to pH 6.5 or 8.0 and held for 48 hours at different temperatures. Disappearance of vanillin is function of solubility (greater at pH 8.0 that 6.5, above 40° C).



Vanillin content in water, adjusted to pH 3.0 or 2.0 and held for 48 hours at different temperatures. Disappearance of vanillin is function of solubility (greater at pH 3.0 that 2.0, above 30° C). Lower levels of vanillin at pH 3.0, below 30° C, reflect precipitation of the compound in the aggregate state.



A schematic view of water structure showing a tight inter-molecular arrangement created by hydrogen bonding of neighboring water molecules.



Solute cavity in water showing disengagement of water structure to accommodate a guest molecule (middle) *

* Martínez JM, Pappalardo RR., Marcos ES, Mennucci B, Tomasi J (2002) Analysis of the Opposite Solvent Effects Caused by Different Solute Cavities on the Metal-Water Distance of Monoatomic Cation Hydrates. J Phys Chem B 106:1118-1123

Maillard Reaction

Inhibitors **Promoters**

F^- Cl^- Br^- I^- ClO_4^- SCN^-

Li^+ Na^+ K^+ Rb^+ Cs^+ NH_4^+

←

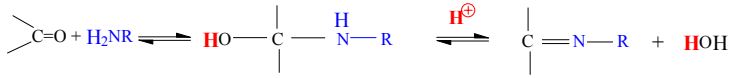
Water Structure Makers (Kosmotropes)

→

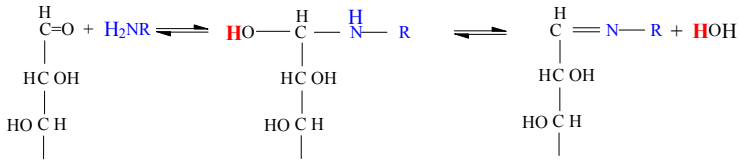
Water Structure Breakers (Chaotropes)

Some ions, which enhance or diminish the structure of water. Water structure-breaking ions are presumed to enhance the solubility and, thereby, the chemical reactivity of vanillin.

Schiff's base formation

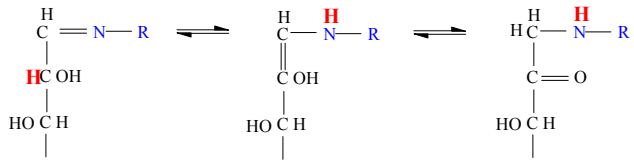


Carbinolamine Schiff's base



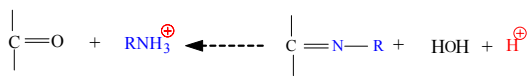
Aldose Carbinolamine Schiff's base

Amadori Rearrangement



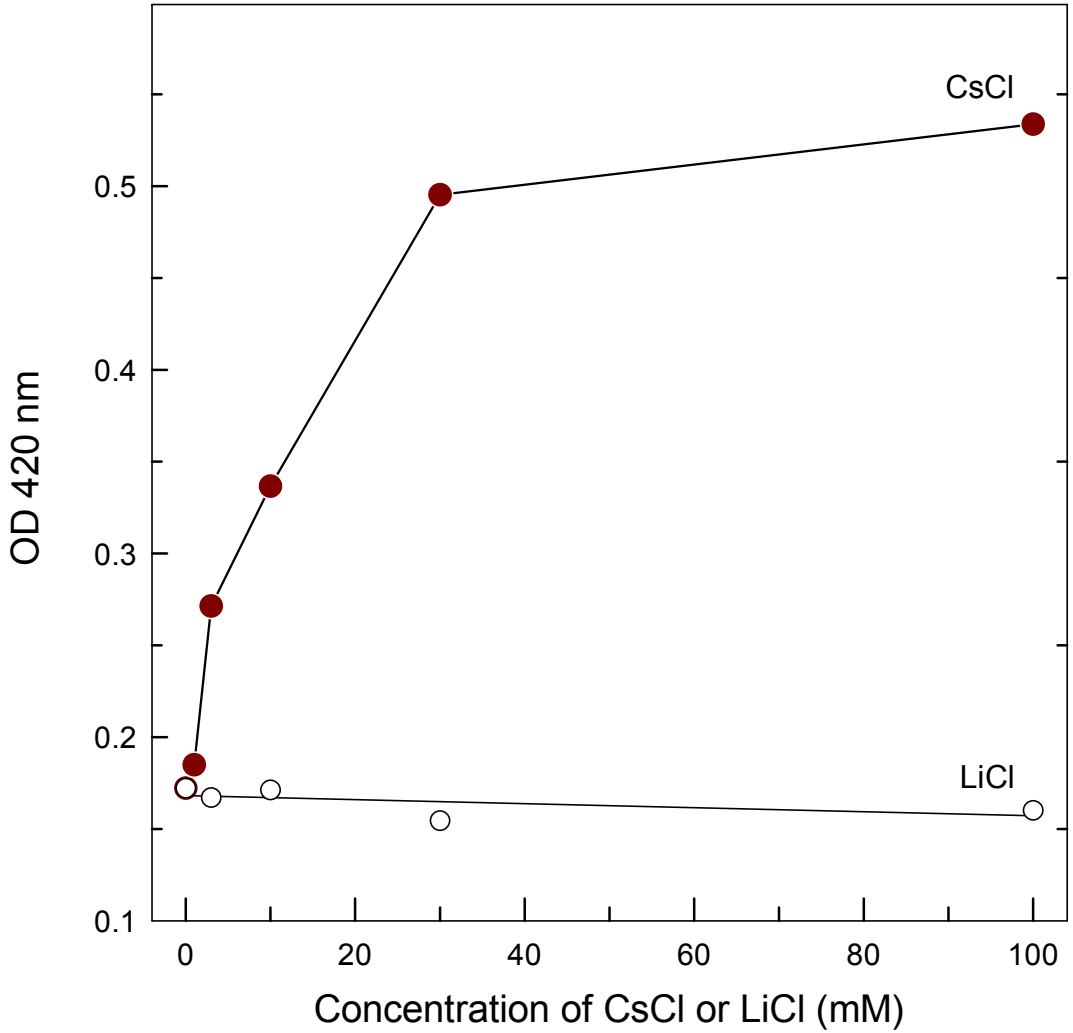
Schiff's base 1-amino-2-keto sugar

Sciff's base Hydrolysis



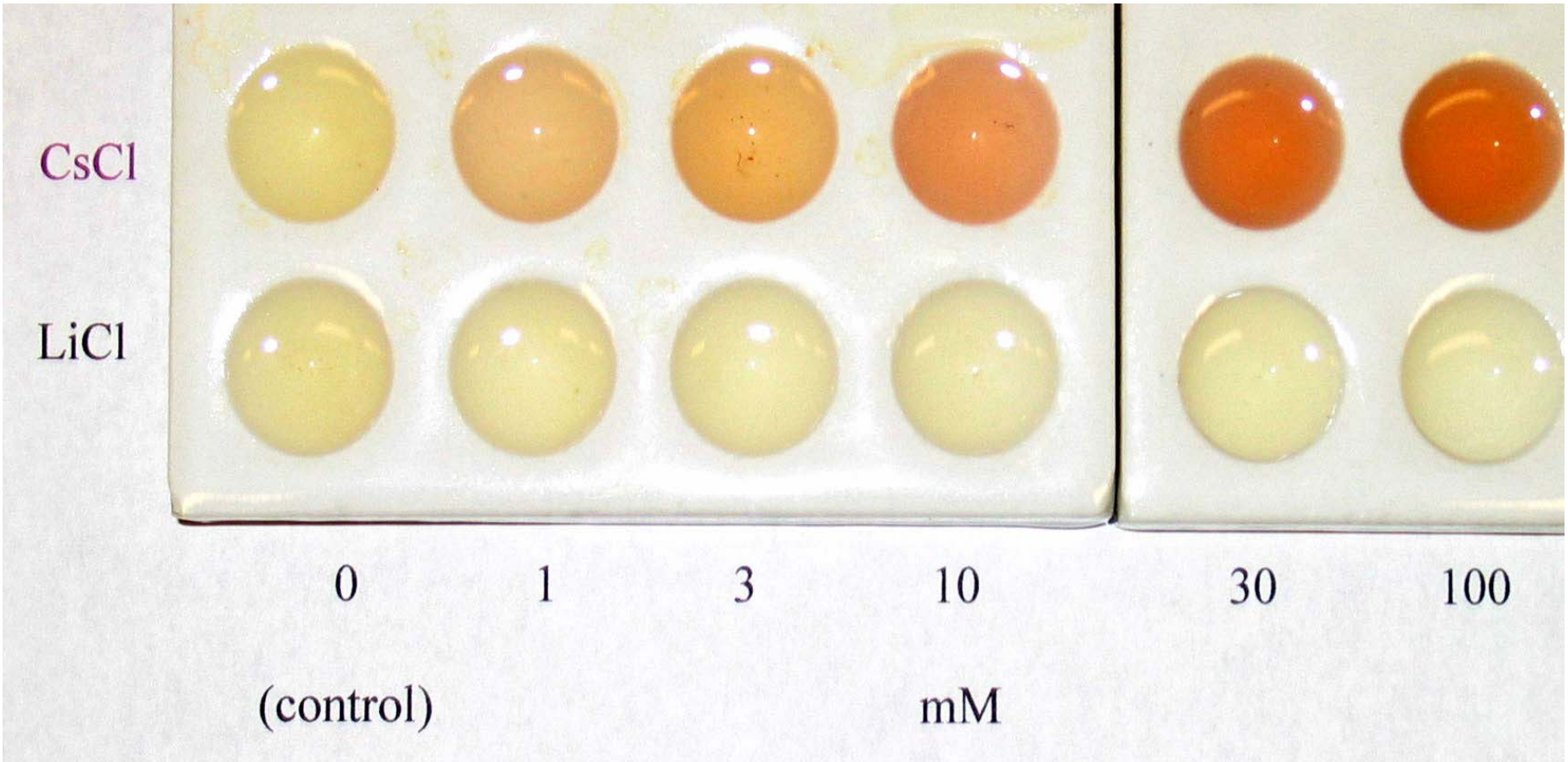
In acid medium Schiff's base will undergo hydrolysis

A generalized scheme of Maillard Reaction showing Schiff base formation followed by Amadori Rearrangement, leading to further degradation including formation of brown color.



Rate of Maillard reaction occurring between vanillin and lysine in presence of varying concentrations of water structure-breaking ions (CsCl) or water structure-maker ion (LiCl).

Solutions containing 5 mM vanillin and lysine adjusted to pH 6.5, held at 65^{o} C for 2 days. Brown pigment formation estimated by spectroscopy.



Visualization of Maillard reaction for vanillin and lysine occurring in absence or presence of varying concentrations of water structure-breaking ions (CsCl) or water structure-maker ion (LiCl).

Summary

Conditions, which increase the water solubility of vanillin (alkalinity or chaotropic agents) enhance water co-volatility and chemical reactivity of the compound.