

Beer's Law, Swimming Pool pH, and Photolysis of OCl⁻

This week we continue with swimming pool chemistry and observe if a swimming pool's disinfectant capacity depends (if there is any dependence) on pH. First, a review of last week's lab results. Last week a standard 250mL 5ppm OCl⁻ solution was exposed for six hours to shortwave UV radiation (254nm). Most results gave a $\Delta[\text{OCl}^-] > 3$ ppm. The average $\Delta[\text{OCl}^-] = 3.5$ ppm, with the range being 1.08 to 4.95 ppm lost. Based on the average $\Delta[\text{OCl}^-]$, more than 60% of the disinfectant capacity- based on [OCl⁻]- for the volume used was destroyed in a comparatively short time period.

The sun's short wavelength UV radiation (collectively called UV-B and UV-C...see box below) is absorbed by ozone, O₃, in the upper portion of the Earth's atmosphere called the stratosphere, which is found extending ~7-30 miles above the Earth's surface (latitude dependent). UV wavelengths >320 nm, the maximum extent of UV-B radiation, are transparent to ozone; that is ozone does not absorb UV radiation greater than ~350 nm. Wednesday's CHM 154 students monitored the $\Delta[\text{OCl}^-]$ over the same time period but using the 365 nm setting on the UV lamp. Their results suggest ($\Delta[\text{OCl}^-] = \sim 3.5$ ppm, average....range from 1.08 to 4.95) that OCl⁻ also strongly absorbs UV at 365nm, a wavelength not filtered out by ozone. UV radiation >350nm reaches the Earth's surface and hence your swimming pool. Bummer.

	UV-C	UV-B	UV-A	
200		280	320	400
wavelength (in nanometers)				

So the question arises: Does a pool's pH affect the absorption of UV radiation (254 and 365nm) and hence the disinfectant capacity? At pH < 4 "chlorine" exists almost exclusively as hypochlorous acid, HOCl. At pH > 9.0 "chlorine" exists almost exclusively as the hypochlorite anion, OCl⁻. Does the slight difference in structure- HOCl vs. OCl⁻- alter the ability to absorb UV radiation? If there is a difference, then this means that pH does play a role in a pool's magnitude of disinfectant capacity.

Measure the absorbance value for a 5ppm OCl⁻ at pH ~4 and pH ~10. This solution has not been exposed to UV radiation.

pH	A
4.0	

10.0

The same OCI^- solution at the same two pH values were exposed for three hours to UV radiation at 365nm. Measure the absorbance value for these two solutions.

pH	A	[OCI⁻]
4.0		

10.0

Determine the $[\text{OCI}^-]$ for each 5ppm OCI^- solution exposed to 365nm UV radiation for 3 hours. Show calculations below and after checking your calculations with Prof. Jennings place the data on the blackboard under the appropriate column. Does pH influence (positive or negative) the photolytic degradation of OCI^- ? If so how? And why?