

Explanation of the Discrepancy between the Florida Department of Environmental Protection's Un-ionized Ammonia Calculator (Version 2.1) and the EPA Text Table 3 Values in EPA 440/5-88-004

The values in Table 3, pg. 31 of the saltwater ammonia criteria document are expressed in mg/L ammonia (molecular weight 17). The Department's un-ionized ammonia calculator (Version 1.2) requires total ammonia to be entered as mg/L ammonia as N (molecular weight 14). The single most obvious source of error or confusion about why the calculator and the EPA table values do not give you the same answer is predominantly due to this different expression of total ammonia.

If the value entered into the calculator is actually total ammonia in mg/L as N, the discrepancy between the table value and the calculator value ranges between 0.002 mg/L and 0.004 mg/L for various pH, temperature, and salinity combinations.

The calculation of percent un-ionized ammonia in a solution of water is dependant upon several variables:

1. Total ammonia
2. Temperature
3. pH
4. molal ionic strength
5. atmospheric pressure.

The stoichiometric acid hydrolysis constant of ammonium ions is also used in the calculation and its derivation is the cause of the discrepancy between FDEP's and EPA's un-ionized ammonia values.

The EPA method, as presented in the saltwater ammonia manual EPA 440/5-88-004 uses equation 21 from Whitman (1974):

$$\begin{aligned} \text{pK}_a^s(T) &= \text{stoichiometric acid hydrolysis constant} \\ &= (\text{pK}_a^s(@ 298^\circ\text{K}) \text{ based on I}) + 0.0324(298 - T^\circ\text{K}), \end{aligned}$$

where $I = (19.9273S)(1000 - 1.005109S)^{-1}$, where S is salinity (g/kg)
= molal ionic strength of the sea water
T = solution temperature in degrees Kelvin.

In other words, the equilibrium constant at some temperature is based upon the equilibrium constant at 25°C with the multiplier 0.0324 applied to the difference between the observed temperature and 25°C. This is based upon observations made by Fuoad (1955) that the response curves in solutions of various molar strength are parallel up to 1 molar strength solutions across temperatures ranging from 0°C to 40°C.

$\% \text{UIA} = 100[1 + 10(\text{pK}_a^s + 0.0324(298 - T^\circ\text{K}) + 0.0415P/T^\circ\text{K} - \text{pH})^{-1}]^{-1}$, where P is atmospheric pressure (default of 1).

The total ammonia value in mg/L NH₃ is then multiplied by the % UIA and the result is the amount of un-ionized ammonia in mg/L NH₃.

The FDEP Un-ionized Ammonia SOP (Revision 2, 02/12/2001) uses a different equation for pK_a^s described in Spotte and Adams (1983) – copied from Thurston (1974, 1979) and Khoo, *et al* (1977)(see references):

$$pK_a^s = 0.0901821 + 2729.2/(T^{\circ}C + 273.2) + (0.1552 - 0.0003142(T^{\circ}C))I,$$

where I = molal ionic strength of the sea water.

This empirically derived equation appears to more directly account for temperature effects rather than simply adjusting the pK_a^s value for temperatures other than 25°C using a conversion factor.

Once the value for pK_a^s is calculated, the value is used to calculate f_s:

$$f_s = 1 / (10^{(pK_{a,s} - pH)} + 1)$$

1/ f_s is the fraction of un-ionized ammonia-nitrogen to total ammonia-nitrogen.

$$(\text{Total ammonia-nitrogen}) * (1/f_s) = \text{mg/L un-ionized ammonia-nitrogen}$$

This is then converted to mg/L un-ionized ammonia as NH₃ by multiplying the mg/L un-ionized ammonia- nitrogen by 17 and dividing by 14.

The 1999 Update of Ambient Water Criteria for Ammonia (EPA-822-R-99-014) for freshwater, presents the equilibrium constant as described by Emerson *et al* (1975):

$$pK = 0.09018 + 2729.2/(T^{\circ}C + 273.2),$$

which is nearly identical to the pK portion of the pK_a^s equation used by Spotte and Adams (1983). Different EPA teams worked on the freshwater and saltwater criteria documents, with the saltwater ammonia criteria team selecting equation 21 from Whitman (1974) over the equation in Spotte and Adams (1983) to use in their 1989 saltwater ammonia criteria document.

References

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