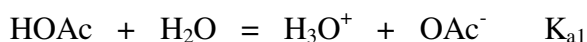


Supporting Information

Following treatment will show that the pK_a values could be used to calculate the concentration of the free base.



$$K = [\text{PhNH}_3^+][\text{OAc}^-]/[\text{PhNH}_2][\text{HOAc}]$$



$$K_{a1} = [\text{H}_3\text{O}^+][\text{OAc}^-]/[\text{HOAc}][\text{H}_2\text{O}]$$



$$K_{a2} = [\text{H}_3\text{O}^+][\text{PhNH}_2]/[\text{PhNH}_3^+][\text{H}_2\text{O}]$$

$$K = K_{a1}/K_{a2} = ([\text{H}_3\text{O}^+][\text{OAc}^-]/[\text{HOAc}][\text{H}_2\text{O}])/([\text{H}_3\text{O}^+][\text{PhNH}_2]/[\text{PhNH}_3^+][\text{H}_2\text{O}])$$

In absence of water there is no self ionization of HOAc and hence $[\text{PhNH}_3^+] = [\text{OAc}^-]$

$$[\text{PhNH}_3^+] = ([\text{PhNH}_2]_T - [\text{PhNH}_2])$$

$$\text{Hence } K_{a1}/K_{a2} = ([\text{PhNH}_2]_T - [\text{PhNH}_2])^2/[\text{HOAc}][\text{PhNH}_2]$$

$$(K_{a1}/K_{a2})[\text{HOAc}][\text{PhNH}_2] = [\text{PhNH}_2]_T^2 - 2[\text{PhNH}_2]_T[\text{PhNH}_2] + [\text{PhNH}_2]^2$$

$$[\text{PhNH}_2]^2 - \{K_{a1}[\text{HOAc}]/K_{a2} + 2[\text{PhNH}_2]_T\}[\text{PhNH}_2] + [\text{PhNH}_2]_T^2 = 0$$

$$x^2 - bx + c = 0$$

$$x = [\text{PhNH}_2]; b = \{K_{a1}[\text{HOAc}]/K_{a2} + 2[\text{PhNH}_2]_T\}; c = [\text{PhNH}_2]_T^2$$

$$x = [b \pm \sqrt{b^2 - 4c}]/2$$

Since K_{a1} , K_{a2} and $[\text{PhNH}_2]_{\text{Total}}$ are known and $[\text{HOAc}]$ is determined experimentally $[\text{PhNH}_2]$ is calculated; a computer program (C++) could be used.

pK_a values: Acetic acid: 4.76; Aniline: 4.60; *m*-methylaniline: 4.71; *m*-aminophenol: 4.31; *m*-chloroaniline: 3.52; *m*-nitroaniline: 2.46; *m*-aminobenzoic acid: 3.07; *m*, *p*-dimethylaniline: 5.17; *m*, *p*-dichloroaniline: 2.96; *p*-methylaniline: 5.08; *p*-methoxyaniline: 5.36; *p*-ethoxyaniline: 5.25; *p*-chloroaniline: 3.99; *p*-bromoaniline: 3.88; *p*-nitroaniline: 1.01; *p*-aminobenzoic acid: 2.41; ethyl *p*-aminobenzoate: 3.33; *p*-aminoacetanilide: 4.60; *o*, *m*-

dichloroaniline: 1.76; *o*-methylaniline: 4.45; *o*-methoxyaniline: 4.53; *o*-ethoxyaniline: 4.47; *o*-chloroaniline: 2.64; *o*-nitroaniline: -0.28; *o*-aminobenzoic acid: 2.09; methyl *o*-aminobenzoate: 2.36; *o*-aminoacetophenone: 2.22; *o*-phenylenediamine: 4.65 (1.86); N-methylaniline: 4.85; N,N-dimethylaniline: 5.15; the value given in parenthesis corresponds to $\text{pK}_{\text{a}(2)}$.