Determination of acid dissociation constants of β-diketones in different solvents

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The acid-base properties of 1-phenyl-3-methyl-4-acyl-5-pyrazolone (HMBP), acetylacetone (HAA) and 1,1'-di-(3-methyl-1-phenyl-2-pyrazolyn-5-on-4-yl)-heptanes (DPH) were studied. β-diketones are weak acids. The strength of an acid is measured by its acid dissociation constant (K_a) or equivalently its pK_a ($pK_a = -\log K_a$).

The constants of acid dissociation were determinate by treatment of experimental data from a potentiometric titration of β-diketones by ethanol solution of KOH. Chloroform, n-butanol, isopropanol, ethanol and water were employed as the solvents. The ionic strength was 0.05-0.1 mol/l KCl electrolyte.

For the β-diketones studied the sequence of decreasing constants of acid dissociation HMBP > DPH > HAA was found. The values of the constants were pK_a=3.95±0.05 for HMBP in ethanol-water solution; pK_a=8.9±0.1 for HAA in water.

The K_a of β-diketones found in n-butanol, isopraponol and chloroform are relative constants of acid dissociation. The pK_a of HMBP, HAA and DPH in n-butanol are lower than that in isopraponol and chloroform. The values of the constants in isopraponol were pK_a=6.10±0.2 (for HMBP); pK_a=8.7±0.2 (for DPH); pK_a=11.9±0.2 (for HAA). The isopraponol is the solvent differentiating. Solvents differentiating are solvents, increasing a difference between constants of balance of process dissociation in comparison with standard solvent (normally it is water).

The values of the constants in n-butanol were pK_a=5.60±0.2 (for HMBP); pK_a=5.8±0.2 (for DPH); pK_a=5.8±0.2 (for HAA). The n-butanol is solvent leveling. Solvents leveling are the solvents reducing a difference between constantan of balance of process dissociation.

In these works, we attempted to interpret the extractability correlation to the pK_a of β-diketones. The constants of extraction (K_{ex}) for complexes of Ca^{2+}, Ni^{2+}, Cu^{2+} with β-diketonates were calculated. The K_{ex} of β-diketonates increases with a decrease of pK_a.