Enthalpies of Solution and Protonation of Free- and Metallo-Porphyrins

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Using a heat flow calorimeter, type Calvet, the standard enthalpies of solution in chloroform of the tetraphenylporphyrin, TPP, tetrakis(4-methoxilophenyl)porphine, TMPP and of the corresponding complexes with Co(II), Ni(II), Cu(II) and Zn(II), were determined calorimetrically. The metal complexes were synthesized as known methods. Their separation was achieved by column chromatography using chloroform as eluent. The solvent was purified and dried just before of the calorimetric measurements. Purity of the porphyrins and complexes was checked 1H-NMR and UV-Vis spectroscopies.

The concentration of each porphyrin solution was 0.0025 $mol \cdot dm^{-3}$, approximately. The values of enthalpies of solution of the studied metalloporphyrins are between 80 $kJ \cdot mol^{-1}$ and 100 $kJ \cdot mol^{-1}$. The enthalpies of protonation of the metalloporphyrins were determined using the same calorimeter but in order to avoid HCl corrosion, hastelloy cells were used.

Dried chloroform was acidified with gaseous hydrogen chloride, then introduced in the calorimetric cells, and used as solvent for the determination of the enthalpies of solution of porphyrin and metalloporphyrin. The formation of the corresponding diprotonated species was verified by 1H-NMR spectroscopy at the end of the calorimetric experiment. All the measurements were made at 303.15 K.