

Potentiometric determination of the pKa of nitrogenous organic bases in acetonitrile medium

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Abstract

The modified acidity constant pKa of benzo[g]- and benzo[f]quinoline containing a tertiary amino group and 4-tropylylated aniline in anhydrous acetonitrile, which has high differentiating properties and a high value of autoprotolysis constant pKs. The modification of the method involves the use of a combined glass electrode with a non-standard internal electrolyte – a saturated solution of potassium chloride in anhydrous acetic acid, which allows potentiometric measurements to be carried out under anhydrous conditions. It is noted that during acid-base titration in anhydrous acetonitrile there are marked jumps in the titration curves, which allows determining the pKa values of organic nitrogenous bases. The basicity series for the nitrogenous nucleophilic centers included in the heterocyclic fragment of the molecules and non-cyclic amino groups of the compounds under study have been constructed. The relationship between the basicity of the heterocyclic fragment and the symmetry of the compound has been established. It is shown that pyridine is the most basic and thermodynamically stable compound. The isomeric forms of benzoquinolines differ markedly in this indicator: the linear form, benzo[g]quinoline, being the least symmetric, the least stable compared to the angular form, benzo[f]quinoline. A similar relationship was obtained for the amino groups of benzoquinolines in comparison with 4-(7-cyclohepta-1,3,5-trienyl)aniline. The evaluation of the accuracy of the measurement method was carried out by comparing the literature and experimental values of the indicator of the acidity constant of a standard compound – pyridine in the same solvent. When calculating the acidity constant of organic bases, the temperature correction was also taken into account according to the Bouxvit formula and the correction for the length of the scale of the solvent used.

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