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Water-acetonitryle solutions features of 1,2,3,4-tetrahydroquinoline derivatives

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Abstract

The results of the study of 1,2,3,4-tetrahydroquinoline solution in water-acetonitrile mixture by potentiometric, conductometric methods and refractometry are given. Acidity and basicity constants of some derivatives of tetrahydroquinoline are determined by potentiometry. The values of the teterahydroquinoline derivatives ionization constants – pKa in the ionization of the carboxyl group and pKb with > NH group ionization were determined experimentally and calculated using MarvinSketch program. A comparison of such data showed good agreement between the calculated and experimental data and demonstrating the possibility of using this program to adequately calculate the values of ionization constants of heterocyclic compounds. It is shown in this case that the change of pH of heterocyclic compounds solutions in water-acetonitryle with a change in the concentration of acetonitrile was due to both the composition of the solution, and the structure of the solutes molecules. It has been demonstrated that the proton-donor and proton acceptor properties of the molecules studied 1,2,3,4-tetrahydroquinoline derivatives determined by nature of the substituent and its position in the molecule, and the influence of the solvent on the displacement of the equilibrium in the solution of these compounds which is manifested through the acidity and basicity constant of solutes and depends on the protolytic properties of the solvent. Displaying pH monotonic increase with increasing concentration of acetonitrile in solution of 1,2,3,4-tetrahydroquinoline, a similar increase in the pH of the solution without dissolved analytes therein, while the corresponding dependence for solutions of 4-carboxyquinoline is considerably more complex character extremal associated probably with the flow of protonation or deprotonation processes in solutions. The dependence of the electrical conductivity of water – acetonitrile solutions of these compounds on the composition of the solution was demonstrated. It was shown plots of experimentally obtained values of conductivity of derivatives of 1,2,3,4-tetrahydroquinoline water – acetonitrile solutions on acetonitrile concentrations. The presence of an extremum on the respective charts, which, according to published data, probably is a result of the association, prototonation or deprotonation processes in solutions.

Determined experimentally and theoretically calculated values of the molar refraction of 1,2,3,4-tetrahydroquinoline were demonstrated. The change of the molar refraction depends on the structure of molecules tetrahydroquinoline derivatives. The presence of negative values exaltation molar refraction, i.e. depression were shown. In this case the data are consistent with the literature, according to which many conjugated heterocyclic systems detect depression molecular refraction – significant negative deviations from the additive caused the existence of intra- and intermolecular interactions. It was shown that the value of the molar refraction for the compounds studied correlated with the values of the polarizability calculated for analyte molecules dissolved in water or acetonitrile, while the relationship between the refraction and the energy of solvation is not so obvious.

References

[1] Yu.Ya. Fialkov. The solvent is a chemical process management tool. *L.: Chemistry*. **1990**. 240p. (russian)
[2] The structural self-organizing in solutions and at interfaces. Ed. Tsivadze A.Yu. *Moscow: LKI*. **2008**. 544p. (russian)
[3] Yu.B. Monakhova, S.P. Mushtakova, S.S. Kolesnikova, L.A. Gribov. *Russ. Jour. analyte. Chem*. **2011**. Vol.66. No.1. P.56-62.
[4] R.D. Mountain. *Int. J. Thermophys*. **2001**. Vol.22. No.1. P.101-110.

[5] O.V. Kharitonova, A.S. Paramonov, S.V. Kurbatova. Acid-base equilibria in water-acetonitrile solutions of nitrogen-containing heterocycles. *Butlerov Communications*. **2009**. Vol.16. No.4. P.31-35. ROI: jbc-02/09-16-4-31
[6] S.A. Dzhabieva, S.V. Kurbatova, Z.P. Belousova, E.E. Finkelstein. Physico-chemical characteristics of triazole derivatives sorption from aqueous acetonitrile solution. *Butlerov Communications*. **2013**. Vol.34. No.4. P.95-101. ROI: jbc-02/13-34-4-95
[7] S.A. Dzhabieva, E.A. Kolosova, I.N. Karaseva, M.O. Karasev, S.V. Kurbatova. Water acetonitrile solutions features of certain aromatic heterocycles. *Butlerov Communications*. **2016**. Vol.46. No.5. P.54-60. ROI: jbc-02/13-34-4-95
[8] T. Mussini, P. Longhi, I. Marcolungo, P.R. Mussini, S. Rondinini. *Fresenius J. Anal. Chem*. **1991**. Vol.339. P.608-612.
[9] B.F. Ioffe. Refractometric methods in chemistry. *Leningrad: Chemistry*. **1974**. 400p. (russian)
[10] V.I. Iwanski. Chemistry of Heterocyclic Compounds. *M.: Higher School*. **1978**. 559p. (russian)
[11] N.A. Nekrasova, S.V. Kurbatova, M.N. Zemtsova. *Sorption and Chromatographic Processes*. **2016**. Vol.16. No.2. P.154-162. (russian)
[12] A.S. Paramonova, S.V. Kurbatova, E.A. Kolosova, M.N. Zemtsova. Potentiometry and conductometry of aqueous acetonitrile solutions of quinoline derivatives. *Butlerov Communications*. **2011**. Vol.26. No.12. P.65-71. ROI: jbc-02/11-26-12-65