Równowagi asocjacyjne alkilopochodnych mocznika i tiomocznika = Association equilibria of alkyl derivatives of urea and thiourea.

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Streszczenie

The studies and comparison of a series of molecular mono- and di-substituted derivatives of urea and thiourea in solvents of increasing polarity are presented [1–4]. These substances are characterized by a high tendency to self-associate through the formation of intermolecular hydrogen bonds due to the presence in their structure both groups as donors (NH) as well as proton acceptors (C=O) or (C=S). Studies were performed by using IR spectroscopy, method of measuring the average molecular weight and the dipole moments. The experimental data were verified by DFT quan-tum chemical calculations with B3PW91 correlation functional. Simultaneous use of these techniques alowed establishing not only the efficiency of aggregation, but also the structure and polarity of formed aggregates. It was shown, that in solvents with weak acidic C-H groups the aggregation was strongly limited because of molecular interactions between solute and solvent. The theoretical DFT calculations which included the impact of the environment on the nature of interactions in the complex were carried out [e.g. Scheme 4.1.4]. A combination of geometry optimization in polarizable continuum model (PCM) with the connection of chloroform molecules (1,2-dichloroethane) with urea dimers enabled to obtain the expected theoretical simulation compliance with the experi-ment.The equilibrium constants were calculated on the basis of data obtained in two independent methods of measurement: IR spectroscopy and measurements of average molecular weights. Good agreement of experimental data of both research techniques were found up to concentration of 0.03 mol/dm3 [Fig. 2.5]. The type of associates have been assessed following the dipole moments measured as a function of concentration, and on the results of density-functional theory (DFT) calculations on the structure and energy of particular species. All of the urea derivatives demonstrated an increase in dipole moment with increased

concentration, suggesting linear-type aggregation [Fig. 4.1.3]. Contrastingly, the dipole moments of the N,N-dimethylthiourea and mono-N-alkyl-substituted thioureas decreased with concentration and suggest that cyclic dimers or trimers are formed by C=S...(HR)2N-C=S interactions [Fig. 4.2.2]. The efficiency of self-aggregation was described by use of two equilibrium constants. The first constant, K1, was describing dimer formation and the second constant, K2, the subsequent multimer formation. In N,N'-thioureas aggregation was lower than for the related urea compounds [Table 4.1.1 and Table 4.2.1].Differences between urea and thiourea derivatives result from the fact that the ureas are stronger bases and, therefore, more active in aggregatio

Słowa kluczowe

model of self-association, Dipole moments, average molecular weight, FTIR spectra, density functional calculations, derivatives of urea and thiourea

model samoasocjacji, momenty dipolowe, średnia masa cząsteczkowa, obliczenia DFT, pochodne mocznika i tiomocznika