



Self-association of N,N'-dialkylthiourea derivatives in non-polar solvents

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ABSTRACT

The paper consists of the joint studies of average molecular weight, dipole moments and the IR spectra of symmetric dialkyl, from dimethyl to dihexyl, thioureas, performed in function of concentration in low polar solvents, with the aim to determine those substances' relative ability of self-aggregation and the form of the subsequent aggregates. The studies were accompanied by the DFT calculations at B3PW91/6-31+G(d,p) level. It was demonstrated that association in CCl₄ and benzene is much stronger than in chloroform and 1,2-dichloroethane, which results from the competition of interaction of acidic C–H groups of solvent molecules with sulfur atom of thioureas. By way of comparing the association constant with the related values for urea derivatives it was shown that the aggregation ability of thioureas is clearly lower than of ureas. This results from the fact that the basicity of sulfur atom is lower than of the oxygen one. Interesting difference between urea and thiourea derivatives is the dependence of dipole moments on concentration, when in urea derivatives dipole moment systematically grow with concentration, showing predominance of near-linear aggregation, in thioureas with shorter chains dipole moments decrease with concentration. Increase the size of chains leads to some preference of linear aggregation – dipole moments increase in non-active solvents. It can be explained by change the conformation in direction of trans–trans forms. Such conclusion was supported by results of DFT calculations.

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1. Introduction

Presented results concern the studies on self-aggregation of symmetric N,N'-dialkyl substituted thioureas in weak polar solvents. A specific feature of this study is that it follows several different methods simultaneously: average molecular weight, dipole moments and the IR spectra measured in function of concentration. Such approach makes it possible not only to estimate the degree of aggregation but also the character/structure of complexes. Thus obtained characteristics are verified by using theoretical methods at B3PW91/6-31+G(d,p) level. The research methods applied in this work are similar to the ones we adopted in the study on self-aggregation of derivatives of urea [1] for that reason the results from both studies may be directly compared.

Derivatives of thiourea are worth attention because of their activity as inhibitors of HIV-1 and HIV-2 Reverse Transcriptases, and their antiviral activity [2–4]. Thioureas derivatives show non-linear polarizability predicting its use in non-linear optics [5,6]. By means of a theoretical method it was demonstrated that replacement of C=O group in urea by its sulfur analog gives a large increase of third-order optical susceptibility [7]. Thiourea and urea derivatives are catalysts in diastereoselective reactions [8]. Since

both groups of compounds possess proton acceptor and proton donor center, they are able to form a variety of complexes with differing structure. Due to directional interactions and relatively high strength of hydrogen bonds they are important moieties in building large aggregates and nanostructures [9].

Symmetric N,N'-dialkylureas tend to form one-dimensional hydrogen bonded chains with coplanar urea moieties. In the case of alkyl derivatives of thiourea, the molecules in the chains are almost perpendicular to one another, and the chains show the zig-zag character. Thioureas can also associate into dimers built of cis–trans monomers, which are relatively more stable than in urea derivatives. Relative stability of trans–trans and cis–trans monomers can be influenced by steric effects of alkylsubstituent of growing bulkiness [10]. N-alkyl derivatives of urea and thiourea form gels in non-polar solvents [11].

The organization of molecules depends on the possible form of hydrogen bonding, however, with the increasing length of N-chains, the importance of the van der Waals interactions is growing. N,N'-dialkylthioureas with the chains shorter than propyl reveal weaker gelling ability than related ureas. The increase of chains length leads to larger gelling ability, whereas the introduction of N-alkyl substituents results in the decrease of melting temperatures. The melting temperature of thiourea (450 K) is higher than for urea (406 K). Thioureas show more complicated pattern of hydrogen bonds organization than ureas. The thermodynamics of fusion and sublimation of solid alkyl ureas and thioureas

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was compared in [12]. Experiments demonstrated that these thermodynamic parameters are different for thioureas and related ureas, which provides evidence of an unequal nature of molecular interactions. It was found that the enthalpy and the entropy of fusion and sublimation are growing with the number of C atoms in N-chains, which points to the significant influence of van der Waals interactions in thioureas – in principle, higher than for analogous alkylureas. Lower values for N,N'-dialkyl derivatives than the N-alkyl ones give evidence to the importance of hydrogen bonding interactions with participation of N–H donor function. Tetramethyl derivatives of thiourea and urea reveal lowering of melting temperatures. These results confirm that the issue of molecular interactions in thioureas in comparison with the related ureas is worth exploring. The intention of the authors is to study that issue in relation to the function of concentration in solutions.

The fundamental differences in aggregation of thioureas as compared with urea result from different proton acceptor and proton donor properties of both molecules. Proton acceptor ability of sulfur is weaker because of the lower negative charge on it, which was calculated by means of various theoretical methods [13,14]. The latter of the aforementioned papers, relying on the analysis of the experimental data from the Crystal Structure Database (CSD), describes weaker interactions of thiourea with water molecule used as a model proton donor. At the same time, lone electron pairs of sulfur have wider directory features than the analogous oxygen compounds (for the former, C=X...H angles are 127–140°, whereas for the latter, the angles equal 102–109°) [14]. That may potentially affect the aggregation of both types of molecules. The inverse abilities of aggregation of ureas and thioureas result from the interactions where these molecules are N–H proton donors, which are stronger for thiourea ($pK_a = 21$) than for urea ($pK_a = 27$). Detailed theoretical analysis of complexes with imines confirmed that prediction [15].

In the study of different patterns and mechanisms of aggregation of thiourea derivatives it was also interesting to explore the self-association of a group of N,N'-dialkylthioureas in function of concentration in a few non-polar solvents and the way it depends on the length of N-chains.

The aim of this study, which applies simultaneously various research methods, was to detect the efficiency and mechanism of the aggregation of N,N'-dialkyl substituted thiourea, as well as to compare the results with previously explored derivatives of urea.

2. Experimental section

2.1. Materials

The research has been carried out using following thiourea derivatives: N,N'-dimethylthiourea – DMTU (Fluka/Acros), N,N'-diethylthiourea – DETU (Aldrich), N,N'-dipropylthiourea – DPTU (Alfa Aesar), N,N'-dibutylthiourea – DBTU (Aldrich), N,N'-dihexylthiourea – DHTU (ABCR GmbH) and solvents: CCl₄ (Riedel-de Haën), C₆H₆ (POCH), CHCl₃ (Aldrich), CH₂Cl₂ (J.T. Baker) and C₂H₄Cl₂ (Lab-Scan).

2.2. Average molecular weights

The average molecular weights were measured in CCl₄, C₆H₆, CHCl₃, C₂H₄Cl₂ solutions by means of the VPO (vapor pressure osmometry) method (Gonotec 070 Osmometer), within the concentration range: 2.55×10^{-3} – 1.2×10^{-1} mol dm⁻³ and using benzil as a standard. The solution and solvent were dropped on two identical temperature sensors. The solvent was additionally condensed on a 'solution sensor' because of the decreased vapor pressure. The

effective concentrations and the effective molecular weights of the solutes were calculated from the differences of temperature of these sensors after their precalibration. The measurements were performed at 40 °C because some limit of vapor pressure is required in this method. Increased solubility at this temperature allows performing measurements at wider range of concentration than at 25 °C.

2.3. Dipole moments

Dipole moments were determined in CCl₄, C₆H₆, CHCl₃, C₂H₄Cl₂ solution at 25 °C in the concentration range: 2.5×10^{-3} mol dm⁻³– 2.5×10^{-1} mol dm⁻³. The electric permittivity of each sample was measured using the heterodyne beat method at 2 MHz on a Dipol-meter WTW DMO1. The densities were determined by means of the Rudolph Research Analytical DDM 2911 Digital Density Meter. For the purpose of performing calculations, the Hedstrand and Onsager methods were followed [16], which assume the additivity of the polarization of the solution. Refraction indices were determined with the help of the Abbe refractometer with the precision of 5×10^{-5} . The molar refraction at the light frequency for sodium lamp – R_D was assumed to be the sum of electron and atom polarization values. That was calculated from the measured refraction indices.

2.4. IR spectra

The IR spectra were recorded on FT-IR Nexus-Nicolet spectrophotometer with the resolution of 1 cm⁻¹ with 128 scans per spectrum in the frequency range of 4000–400 cm⁻¹ at the temperatures of 25 °C and 40 °C. The Happ-Genzel apodization setting was applied for the sample and background collection. The temperature of the sample was regulated by the automatic Graseby Specac controller. Samples were examined in carbon tetrachloride, chloroform and dichloromethane solutions using a 0.053–1025 mm-thick cesium iodide cell, a 2.93 mm potassium bromide cell and a 0.2–0.5 mm KRS-5 cell (in 40 °C) for which background was taken into account. The IR spectra were taken within the range of concentration which approximately coincided with the concentrations used in the measurements of dipole moments. In order to remove the fluctuating baseline and the mathematical resolution of bands, the data were processed using Grams 32/AI Software (Galactic Ind. Corp.). An additional condition in the conducted measurements was to preserve the constant level of the product of concentration and thickness, since that provides a constant number of molecules in light pass. In that way, the modification of spectra in function of concentration can be clearly seen, while the bands which do not change with concentration may document the precision of the measurements.

2.5. DFT calculations

The experimental data were compared with quantum chemical calculations carried out at the B3PW91/6-31+G (d,p) level of theory [17,18]. The hybrid B3PW91 method combines Becke's three-parameter functional with the non-local correlation provided by the Perdew-Wang expression. According to reports [19,20], only hybrid functionals can provide an accurate description for the systems with hydrogen bonds. No scaling factors have been used for improving the agreement between the experimental and theoretical wavenumbers. The calculations, tending towards an optimized structure of single molecules and polymeric species as well the frequencies and intensities of the corresponding modes, were performed using the Gaussian-09W program [21].

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