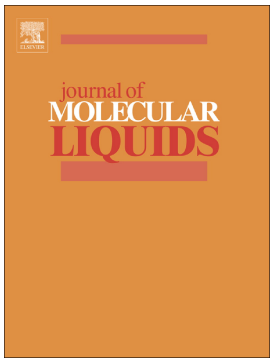

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Investigation of steric effect in the formation of hydrogen-bonded complexes of isomeric chlorophenols with N,N-dimethylaniline

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Abstract

In order to study the steric effect in the formation hydrogen bonded complexes two systems were chosen. The formation of hydrogen bonded complexes of N,N-dimethylaniline (DMA) with o-chlorophenol (o-CP) as well as m-chlorophenol (m-CP) in tetrahydrofuran medium is established by ultrasonic and UV spectral methods. Ultrasonic velocity (u), density (ρ) and viscosity (η) are measured for the two systems in the concentration range 0.01M-0.1M and acoustical and excess thermo acoustical properties are computed. The trend in the acoustical and excess parameters with concentration in both the ternary systems establishes the formation of hydrogen bonded complexes between tertiary amine (DMA) and the two chlorophenols. The formation constants (K) of the hydrogen bonded complexes are reported and compared with those obtained by UV spectral method. It may be pointed out that trend in K values obtained by acoustical method is the same as that obtained by optical method. Experimentally obtained K values are correlated with the molecular properties of chlorophenols computed using B3LYP/6-311++G(d,p) basis set. The geometry, bond characteristics and interaction energies of the hydrogen bonded complexes were investigated through quantum chemical calculations. The computed values of molecular properties explain the trend in the experimental 'K' values of the two complexes. It is found that complex of ortho-Chlorophenol (o-CP) with DMA is thermodynamically less stable than the DMA-meta-Chlorophenol (m-CP) complex indicating the steric influence of chloro substituent near the site of complex formation.

Key words: Hydrogen bonded complexes; steric effect, ultrasonic; UV spectral methods, DFT analysis

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