

The Jan Kochanowski University in Kielce
Faculty of Mathematics and Natural Sciences
Institute of Chemistry

ABSTRACT OF Ph.D. THESIS

„Influence of intermolecular interactions in solutions on changes in dipole moment and Kerr constant of selected chemical compounds”

Author of dissertation: mgr Karol Olan

Dissertation supervisor: dr hab. Walentyna Zubkowa, prof. UJK

Auxiliary supervisor: dr Agnieszka Puchała

Introduction. Intermolecular interactions have an essential role during various type of chemical, physical and physicochemical phenomena. Often these interactions are of electrostatic nature, what makes it possible to describe them using the most important parameters, which characterize electrical properties of molecules: polarizability (α) and dipole moment (μ). These parameters determine van der Waals interactions that contribute to adhesion and cohesion forces. They are responsible for adsorption, extraction, solvation etc.

Not less important for the analysis of intermolecular interactions is the information about molecular polarizability anisotropy and polarizability ellipsoid, which have been studied less because of the problems with the use of electrooptical research methods and the need for determination of molar Kerr constant (mK).

The data described in literature refer mainly to the interactions between molecules of pure substances. Interactions in mixtures of substances and solutions of organic compounds in polar and non-polar solvents also have been studied to a lesser extent. A serious research problem is to determine intermolecular interactions for low volatile compounds. Various models for determination of the potential of intermolecular interactions have been described in the literature. A large number of models indicates the diversity of intermolecular interactions taking place and the lack of universal model that allows us to describe intermolecular interactions more precisely and characterize the changes in organic compound systems under the influence of various factors. All aforementioned made me present the subject at issue as in the literature along with further discussion and own improvements developed in my Ph.D. thesis.

The main aim of my doctoral thesis was to establish a correlation between the values of electrical properties (μ , mK) and the potential of intermolecular interactions. In my investigation I focused on six research tasks: the analysis of references to models of local field, the studies on

intermolecular interactions between solute and solvent, a comparative analysis of experimental and calculated values of μ and mK , the development of a new method to estimate the values of μ and mK for isolated molecules, the application of discrete-continuum model of solvation to the description of intermolecular interactions in solutions, and on establishing a correlation between experimental values of μ and mK and the electronic structure of investigated compounds – five-membered cyclic imides.

Methodological part of my doctoral thesis includes a description of reagents and studied compounds. I used twenty six compounds for the studies on the dipole moment and twenty three compounds for the studies on molar Kerr constants. In addition, I studied ten five-membered cyclic imides and six 4-aryl-1,3,5,7-tetramethyl-bis-pyrazole[3,4-e;4',3'-e]pyridines synthesized by me. Moreover, I justified the use of primary formulas for calculation of investigated properties. I used Hedestrand method to obtain the values of μ and Le Fevre method for values of mK .

Performed research. To reach the selected goal, I studied intermolecular interactions and potential dependency of dipole moment determined by Hedestrand extrapolation method in polar solute vs. non-polar solvent systems. The same extrapolation method I used to investigate the changes in dipole moment in polar solute vs. polar solvent systems. I conducted the studies on intermolecular interactions and potential dependency of molar Kerr constants in non-polar solvents with Le Fevre extrapolation method. Obtained molar Kerr constants were applied to determine appropriate values in accordance with local field models suggested by Zamkov and Vuks. The last part of my research was the analysis of the influence of electronic structure of five-membered cyclic imides on experimental deviation of μ and mK on the basis of values calculated by additive schemes.

Main conclusions

I proposed and checked a new simple method of determination of μ values of isolated molecules from solution measurements. I synthesized six 4-aryl-1,3,5,7-tetramethyl-bis-pyrazole[3,4-b;4',3'-e]pyridines (four of them are not described in the literature on subject) and confirmed their structure with FT-IR and ^1H NMR spectroscopy. I determined the values of μ for twenty six compounds in non-polar solvents and seven compounds in polar solvents.

I stated linear correlations between the values of μ and the potential of intermolecular interactions in non-polar solvents. I also determined non-linear correlations between values of μ and potential of intermolecular interactions in polar solvents. From analysis of experimental data on μ of 4-aryl-1,3,5,7-tetramethyl-bis-pyrazole[3,4-b;4',3'-e]pyridines, I stated that the character of substituent has no influence on correlation between μ and potential of intermolecular interactions for 4-aryl-1,3,5,7-tetramethyl-bis-pyrazole[3,4-b;4',3'-e]pyridine-non-polar solvent systems. I suggested that specific intermolecular interactions cause the deviation of correlation.

I proposed the method of extrapolation to zero value of intermolecular interactions potential, which can be used to detect specific intermolecular interactions in studied systems. I determined mK values using three models of local fields for twenty three compounds in seven non-polar solvents. I found a correlation between the values of mK and the intermolecular interaction potential in non-polar solvents. I proposed and checked a new simple method of estimation of mK values in the gas phase from solution measurements. I achieved the best agreement with experimental results by application of the model of local field that was proposed by Zamkov. I obtained a correlation between the deviation of μ and mK from the values calculated in accordance with the additivity rule and electronic structure of five-membered cyclic imides. The results and discussion presented in my doctoral thesis suggest the existence of strong interaction between the atoms in imide group, imide group itself, and other molecular fragments in molecules of five-membered cyclic imides.