Density Functional Theory a tool to study the Interactions Behaviour Among Binary Mixtures of Alkoxyalkanol and Amides : A Review

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ABSTRACT

Density functional theory (DFT) has progressively emerged now-a-days a leading tool for modelling and simulation of chemical systems. The basic notion in the density-functional theory of many electron systems is that the energy of an electronic system can be expressed in terms of its density. Ab-initio & DFT calculations are being used to assess the extent of existing intermolecular hydrogen bonding. Various hydrogen-bonded complexes of alcohols/alkoxyalkanol with different proton accepting and proton donating molecules have been modelled using DFT with hybrid B3LYP. The characteristics of complexes are influenced not only by the principle hydrogen bond of the O---H with the proton acceptor heteroatom, but also by additional hydrogen bonds of C---H moiety with alcoholic oxygen as a proton acceptor. In a protic solution, the intra-molecular hydrogen bond may disrupt in favor of two solute-solvent intermolecular hydrogen bonds. The balance of the increased internal energy and the stabilizing effect of the solute-solvent interactions regulates the new conformer composition in the liquid phase. Moreover, a general correlation has been observed in-between the binding enthalpy and the electrostatic potential at the hydrogen center participating in the formation of the hydrogen bond. In this review, some historical landmarks in the development of DFT have been outlined, emphasizing on its main characteristic being an electron density-based theory.

Keywords : Density Functional Theory, Physicochemical properties, Hydrogen bonding , Molecular interactions

I. INTRODUCTION

The nature of intermolecular interactions and the physico-chemical properties of the solute, solvent studied are diverse studies of thermodynamic

properties of solution can be studies via experimentation. The measured thermodynamic properties acquired are the essential basis for the development of empirical, semi-empirical or theoretical models employed to represent and predict the behaviour of fluids [1-7]. The volumetric properties of solutions have proven to be a very useful tool in elucidating the structural, interactions (i.e., solute-solvent, solute-solute, and solvent-solvent) occurring in solution, because they provide an indirect insight into the conformational feature of the components in solution. Precise calculations of densities and refractive indices of solutions have immense significance in designing engineering processes in chemical and biological industries [8-9]. The density, refractive index and thermodynamic parameters have been widely utilized to examine different kinds of association, extent of molecular interactions and molecular packing in solutions. In addition, these properties are also used to check the applicability of differential data and give the information regarding the nature and extent of molecular interactions in solution. Apparent molar volumes and limiting apparent molar volumes of dilute solutions are useful parameters for the development of molecular models to describe the thermodynamic behaviour of solution. Thermodynamic properties of liquid mixtures can be utilized to extract information about the existence of intermolecular interactions among the constituents of mixtures. The knowledge of thermodynamic properties is essential for the proper design of industrial processes, chemical engineering etc. and for optimizing thermodynamic model/theories development. Excess properties of liquid systems, such as molar volumes, are required for testing the theories of solutions, development of separation techniques and equipment, and for other industrial applications. For these reasons the collection of experimental data not only increases the empirical knowledge by creating a database, but it is also useful for better generalization of models of the solvent, and binary (or more complex) systems. These are interesting challenges for chemists, physicists, engineers, biotechnologists and many other researchers working in different fields. The composition and temperature dependences of the volumetric properties of multi-component liquid mixtures have proved to be a useful indicator of the existence of significant effects resulting from intermolecular interactions [16-17]

The physico-chemical properties (density, viscosity, refractive index or speed of sound and the thermodynamic behaviour of binary mixtures) have been studied for various reasons. One of the most important of which is that these properties provide information about molecular interactions. Many engineering problems require quantitative data of the viscosity and density of liquid mixtures. Such data find extensive application in solution theory and molecular dynamics [18]. Furthermore, these properties are used for the interpretation of data obtained from biochemical and kinetic studies [19]. As the excess thermodynamic functions are sensitively dependent on different in intermolecular forces and size of the molecules, so these properties have been widely used to study the intermolecular interactions between the various species present in the liquid mixtures.

The appropriate design and development of separation processes in the chemical industry are accustomed by a sufficient knowledge of physico-chemical properties of liquid mixtures. An examination of the literature [10] demonstrates few available measurements of physical properties for binary mixtures of Dimethyl formamide (DMF) with 1-alkanols at single temperature (lower 1-alkanols and higher 1-alkanols and even less at numerous temperatures [11-14]. The excess properties of binary mixtures of N,N-dimethylformamide with 1- octanol, 1-nonanol and 1-decanol using experimental data have been reported [15].

The composition and temperature dependence of excess properties of binary liquid mixtures provides extensive information regarding the intermolecular interactions between the component molecules. These thermodynamic properties at different temperatures and concentrations of pure chemicals and their binary liquid mixtures over the whole composition range are useful for practical chemical engineering purposes and many biological systems. Clearly, over the years, there has been considerable advancement in the experimental investigation of the excess thermodynamic properties of liquid mixtures in the chemical industry. Studies on different physicochemical and thermodynamic properties of liquid binary mixtures within wide ranges of compositions and temperatures are important sources of information that may be used to examine the relationship between the internal structure of the system, nature of intermolecular interactions, and the physical properties of the mixed solvent studied.

Density functional theory (DFT) has progressively emerged in recent decades as a reliable tool for modelling and simulation of chemical systems. The computational chemistry is unquestionable and joining hands with experimental chemists. With advancement in the computational chemistry-based software the Density-functional theory (DFT) now a days is the most successful approach for optimization of the electronic structure of matter [20-23]. The success of the theory is largely based on the fact that many DFT approximations can predict properties such as thermochemistry, kinetics parameters, spectroscopic constants, and a large range of properties with an accuracy rivalling those obtained by high-level *ab initio* wavefunction theory methods in terms of agreement with experimental quantities [24]. Despite of the success in predicting many chemical and physical properties, the conventional density-functional approximations have well-known shortcomings [25-26]. In recent years, a great deal of attention has been paid to the inability of conventional DFT methods to predict dispersion interactions accurately.

Before focusing on DFT, it is worthwhile to recall the basic features of ab initio methods traditionally used in quantum chemistry. The common goal of conventional ab initio methods consists in solving the Schrodinger equation, within the Born– Oppenheimer approximation:

$$\hat{H}\Psi = E\Psi \qquad (1)$$

H is the Hamiltonian of the system

$$H = T_e + V_{ee} + V_{ne} + V_{nn} \qquad (2)$$

where T_e, V_{ee}, V_{ne}, And V_{nn} are the kinetic energy, electron— electron repulsion, electron— nucleus attraction, and nucleus— nucleus repulsion operators, respectively. E is the total energy, and Ψ is the N-particle wavefunction. The term ab-initio means that no empirical parameters are introduced to solve Eq. (1). Practically, the fundamental principles of most ab-initio methods are based on the Hartree— Fock (HF) approximation, which is central to chemistry. Within this approximation, the wavefunction Ψ is represented using a Slater determinant of one-electron wavefunctions Ψ_i, leading to the HF equations

$$\left(-\frac{1}{2}\nabla^2 + v_{eff,i}^{HF}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \qquad (3)$$

where ∇^2 is the laplacian operator and $v_{eff,i}^{HF}$ is the effective HF operator:

$$v_{eff,i}^{HF}(r) = v_{ext}(r) + v_H(r) + v_{x,i}^{HF}(r) \qquad (4)$$

In Eq. (4) , v_{ext} , v_H , and $v_{x,i}^{HF}$ are the external, Hartree, and non-local exchange potentials, respectively. ε_i is the eigenvalue of electron i in spin—orbital Ψ_i .

Approximate Wavefunction

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_1(x_2) & \cdots\cdots & \chi_1(x_N) \\ \chi_2(x_1) & \chi_2(x_2) & \cdots\cdots & \chi_2(x_N) \\ \cdots & \cdots & \cdots & \cdots \\ \chi_N(x_1) & \chi_N(x_2) & \cdots\cdots & \chi_N(x_N) \end{vmatrix}$$

$$\chi_i(r,\sigma) = \phi_{i\alpha}(r)\alpha(\sigma) \qquad or \qquad \chi_i(r,\sigma) = \phi_{i\beta}(r)\beta(\sigma)$$

Energy

$$\langle H \rangle_{HF} = \sum_{i,\sigma_i} \langle \phi_{i\sigma_i} | \left(-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) \right) | \phi_{i\sigma_i} \rangle + \frac{1}{2} \sum_{i,\sigma_i;j,\sigma_j} \iint \frac{|\phi_{i\sigma_i}(\vec{r})|^2 |\phi_{j\sigma_j}(\vec{r_1})|^2}{|\vec{r}-\vec{r_1}|} d\vec{r}d\vec{r_1}$$

$$-\frac{1}{2}\sum_{i,\sigma_i;j,\sigma_j}\delta_{\sigma_i,\sigma_j}\iint\frac{\phi_{i\sigma_i}(\vec{r})\phi^*_{j\sigma_j}(\vec{r_1})\phi_{i\sigma_i}(\vec{r_1})\phi_{j\sigma_j}(\vec{r})}{|\vec{r}-\vec{r_1}|}d\vec{r}d\vec{r_1}$$

The problem is that HF does not account for electron correlation due to the rigid form of the single determinant wavefunction. Indeed, to solve the HF equations, the assumption has to be made that each electron interacts with the average potential generated by the other ones, neglecting thus the instantaneous repulsion (i.e. the Coulomb correlation). To take correlation into account, it is necessary to go beyond the HF approximation and to make use of the so-called post-HF methods, such as configuration interaction, coupled-cluster or Mgller—Plesset perturbation theory [27]. In post-HF methods, the wavefunction is generally represented by a linear combination of determinants accounting for correlation. Moreover, whereas the post-HF methods offer a systematic way to improve the accuracy of the results, they scale as fifth or even higher power with the size of the system, implying then a considerable computational effort.

For these reasons, density functional theory is now-a-days a valuable alternative for including correlations effects, without using intricate wavefunctions methods. Indeed, the basic idea of DFT is to replace the complicated N-electron wavefunction by the electron density p as a basic local variable. As demonstrated by the theorems of Hohenberg and Kohn [28], this fundamental change of variable can be done without loss of rigor. These authors proved, indeed, that the electron density p can determine, in a unique way, all the properties of the system. They also demonstrated that the total energy of the system is stationary with respect to the density p (i.e. the minimum of the total energy functional 6[p] is obtained when evaluated using the exact density of the ground state). Unfortunately, the Hohenberg—Kohn theorems do not provide the exact form of the total energy functional *E[p]*. Among the different components of the total energy, the exact density functional forms of both kinetic and exchange-correlation terms remain unknown. To circumvent the problem of the kinetic part (much larger than the exchange- correlation one), Kohn and Sham (KS) [29] proposed to introduce a set of fictitious one-electron wavefunctions J; to build a Slater determinant.

$$\left(-\frac{1}{2}\nabla^{2} - v_{eff,i}^{HF}(\mathbf{r}) \right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \qquad 6$$

Interestingly, DFT has been first applied to solids, with a rather late recognition by chemists and molecular scientists. The interaction behaviour between the molecules can be established from study of characteristics abrupt departure from ideal behaviour of some physical properties viz. enthalpies and spectroscopy-IR , NMR[1].

$$\left(-\frac{1}{2}\nabla^2 + v_{eff,i}^{HF}(\mathbf{r}) \right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \qquad 7$$

Inclusion of exchange and correlation energies via wave functional approach is very difficult, particularly if the number of electrons becomes large.

Density-Functional Theory provides an alternate method by reformulating the many-electron problem in terms of its density. Whereas in wave functional approach a large number of orbitals in terms of 3N

coordinates of N electrons are involved, in density-functional theory only one variable – the density of electrons – in terms of only 3 coordinates in involved.

Spectral implementations of DFT

Now a days the density functional theory (DFT) approaches employed into quantum- chemical computational programme find wide application and usefulness in Spectroscopic analysis of frequencies and spectral intensities for interpreting the experimental spectra of molecules. The *DFT with hybrid B3LYP* programme have successfully been used for calculation of the molecular and electronic structures of ground-state systems and various spectral parameters related to NMR, ESR, UV-Vis and IR [30]. DFT methods give satisfactorily high accuracy of normal mode calculations as the limitations of the harmonic approximation are often a foremost cause of divergence between theory and experiment values. Anharmonicity and hydrogen bonding are two aspects that can be reasons for discrepancy that result in a lower frequency for a specific normal mode than projected by harmonic approximation [31]. The DFT methods have paved the way to overcome the errors arises due to electron correlation and anharmonicity of the vibrations in interpreting the experimental conclusions and to generate the optimized geometry [32, 33]. Computation of vibrational spectra of molecules in their ground and excited states can be done by using the Gaussian program. The program can also designate the dislocations of the molecule as it undergoes normal modes of vibrations along with prediction of spectral frequencies and intensities. The spectra can be produced from a list of frequencies and intensities employing a Gaussian broadening function as depicted in Eq

The vibrational frequencies of the pure and equimolar H bonded systems have been calculated using the Hartree -fork self- consistent field method & Density Functional Theory (DFT-B3LYP) methods with 6-

31+G* and 6-311+G** basis sets using Spartan 08 modelling software[34]. The vibrational frequencies during the formation of hydrogen bond in equimolar binary mixtures of NN-dimethylacetamide with propane-1-ol/prppane-2-ol are supported by the experimental FT-IR measurement data[35].

The molecules of alkoxy alkanol are self-associated in pure state through intra molecular hydrogen bonding and amide being non-aqueous solvent since it has no hydrogen bonding in pure state. Therefore, amide acts as an aprotic protophilic medium with high dielectric constant and it is considered as a dissociating solvent. Thus, the addition of amide in the mixture causes dissociation of hydrogen bonded structures. In a study proposed by [35] the addition of alcohol (1PN/ IPA) with N,N-dimethy acetamide causes dissociation of hydrogen bonded structure of alcohol (1PN/IPA) and subsequent formation of new hydrogen bond (–C=O….HO) between proton acceptor oxygen atom (with lone pair of electrons) of –C=O in DMA group and hydrogen of HO– in alcohol (1PN/IPA) group. The internal pressure, in both the systems, is observed to be increasing with increase in the concentration of alcohol (1PN/IPA). The increase in internal pressure generally indicates the association of molecules through hydrogen bonding and thereby, it supports the present investigation[36].
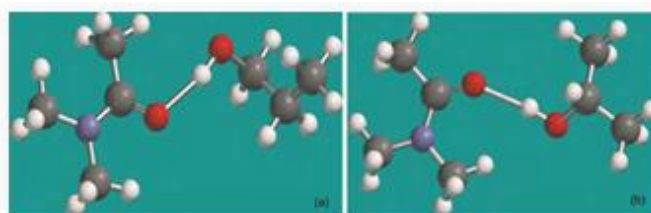

Fig -1 DFT Optimized geometrical structure of : (a) DMA + propan-1-ol, (b) DMA + propan-2-ol

The density functional theory at DFT-B3LYP/6–31 + G (d,p) level is compatible for geometry optimization without introducing the conformational changes evident from the fair agreement between theoretical

and experimental spectral characteristics (IR, NMR and UV–Visible)[37]

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