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Computational Investigation on Excess Molar Volumes and Enthalpies at Infinite Dilution of Host–Guest Interaction in Gas Hydrates

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Abstract*—In the literature, thermochemical properties were determined by using quantum chemical calculations for systems containing hydrates and H_2, N_2, O_2, CO, CH_4 and NH_3 gas molecules, to examine the effect of the size of gas molecules on excess partial molar function of hydrates. The excess partial molar volumes, $V_i^{E,\infty}$ and enthalpies, $H_i^{E,\infty}$, at infinite dilution of the binary mixtures were computed by ab initio method at the M05-2X/ 6-311++G** level of theory using PCM theory in the liquid phase. Computational results help to clarify the nature of the intermolecular interactions in host (hydrate) + guest (H_2, N_2, O_2, CO, CH_4 and NH_3) complexes.$V_i^{E,\infty}$ values of solutions including polar gas molecules are higher than those of mixtures with unpolar gas molecules.

***Index terms* -Ab initio, hydrate, guest, Excess partial molar volumes at infinite dilution, Excess partial molar enthalpy at infinite dilution.**

I. INTRODUCTION

It is crucial to researcher the study of gas hydrates for the different application as a gas storage material and in environments [1-4].Gas hydrates provide porous structures for encaging gas molecules and have become very popular recently especially to improve industrial gas storage and a transportation medium [5-7]. Further, on the basis of a previous study, thermodynamic properties were used to study interaction between host water cages and guest molecule [8-10].

Naturally gas hydrates have clathrate structures that were generated much interest in the study of the storage materials in which small atoms/molecules gas such as methane, nitrogen, and carbon dioxide are trapped inside a polyhedral water cage of different sizes.Water complexes consisting of 12 pentagonal rings made up of 20 water molecules, in particular, are the heart of ongoing studies due totheir broad significance ranging from biological to chemical systems [11-13].

The guest (light gas) and host (water) complexes successfully developed are based on noncovalent interactions between guest and water-type functionalities. At this time, reliable quantitative information on the thermochemical properties of the host-guest complexes is quite limited.In addition, there is a strong interest in calculating the thermodynamic behavior of these complex systems. In Gas hydrates, an ice-like material, careful thermodynamic consideration is necessary to accountthermodynamically favorable conditions which gas hydrates are stable. It may be noted that the related experimental results are scanty. The thermodynamic perception of the strength of host–guest interactions is expressed through the utilization of excess thermodynamic properties which are served as a valuable tool for this purpose[14-16]. These properties have been applied as a qualitative guide to predict the complex formation in these mixtures. The thermodynamic properties of infinitely dilute solutions is confirmed that been very difficult to predict and systems involving these conditions should always have the results from computational work validated by experimental data. The capability of infinite dilution excess molar enthalpy data is to accurately determine vapor-liquid equilibria (VLE) and also the infinite dilution activity coefficient [18]. As the infinite dilution partial molar excess functions correspond to a transfer of the solute from its pure liquid state to a hypothetical infinitly dilute solution of unity solute mole fraction x_1 =1, are of great importance in understanding the nature of molecular aggregation that exists in the binary mixtures. The resulting experimental processto obtain thermodynamic values is very time-consuming and may require a substantial cost which could be much higher than the cost required for computational study.

II. RELATED WORK

It is a subject of great interest and significance in computational and theoretical chemistry to determine the excess functions and intermolecular interactions for mixtures, with the aim of correlating the structural and thermodynamics aspects [19-22]. The host–guest interaction between a dodecahedral water cage and a variety of guest species was reported at the MP2/CBS limit [23].The different theoretical and computational approaches such as ab initio methods and thermodynamics procedures have been employed to determinate thermodynamics properties of host–guest complexes [**Error! Bookmark not defined.**].

In this study, thermodynamic measurements were made for the host (hydrates) + guest (light gas) complexes to recognize the existence of interactions between molecules and of structural effects in the mixtures under study which were calculated from the computational data.

The excess partial molar volumes and enthalpies at infinite dilution for the mixtures of gas hydrates were calculated at liquid phase using the M05-2X/6-311++G** density functional theory (DFT) [25] by PCM (polarizable conductor model) method [26]. Polarizable Continuum Model, PCM, is now widely used to describe hydration in conjunction with quantum mechanical calculations that simulates the solvation process by embedding the solute inside a cavity surrounded by the solvent.

The estimations of hydrate properties such as set of computational excess molar enthalpy and volume at infinite dilution for various gas molecules are quite important. Excess partial molar volumes at infinite dilution ($V_i^{E,\infty}$) and enthalpies at infinite dilution ($H_i^{E,\infty}$) of host (hydrates) + guest (H_2, N_2, O_2, CO, CH_4 and NH_3) complexes in aqueous phase studiedmixtures were computed by using the M05-2X/6-311++G** density functional theory (DFT) [27],the estimation of the solvent effects was attempted by using the self-consistent reaction field (SCRF) and more elaborate polarizable continuum (PCM) models [28].

II. COMPUTATIONAL METHODS

Firstly, the geometries of host (hydrates) + guest (H_2, N_2, O_2, CO, CH_4 and NH_3) complexes were optimized using the Gaussian 03 program [29-31] by the M05-2X density functional theory (DFT) paired with the 6-311++G** basis sets. The optimized representative geometries of the involved mixtures are displayed in Figure 1. Further, the optimized structures also serve as the reference structures for frequency calculations. Thermochemical calculations were determined using harmonic ab initio frequencies on the same level of theory as used for all complexes. In the next step, $H_i^{E,\infty}$ and $V_i^{E,\infty}$ of included systems was calculated.

According to this treatment, the excess molar enthalpies and volumes at infinite dilution $X_1^{E,\infty}$ (X = H or V) can be computed as equation 1:

$$X_1^{E,\infty} = X_{alkanol+BnOH}^{sol,\infty}(solvent\ alkanols) - 1/2\, X_{alkanols+alkanols}^{sol,\infty}(solvent\ alkanols) - 1/2\, X_{BnOH+BnOH}^{sol,\infty}(solvent\ BnOH) \quad (1)$$

Where $X_i^{E,\infty}$ excess partial molar enthalpies and volumes at infinite dilution of host (or guest) component refers to changes in enthalpies and volumes of solution when passing from pure liquids $X_{host+host}^{sol,\infty}$ (or $X_{guest+guest}^{sol,\infty}$) to their mixtures $X_{host+guest}^{sol,\infty}$ [32-35]. The values of $X_{guest+guest}^{sol,\infty}$, $X_{host+host}^{sol,\infty}$ and $X_{host+guest}^{sol,\infty}$ were computed through frequency and single point calculations in aqueous phase on the optimized geometries using equation 2. The excess molar enthalpies and volumes are the difference in the strength of interactions between unlike species (host/guest) and like species (host/host and guest/guest) so that enthalpy and volume of like components which were considered as dimers was divided by two. It is clear that pure component should be considered as dimers.

Environmental effects on the properties of these mixtures were modeled by the self-consistent reaction field (SCRF) method using a polarizable continuum model (PCM). In this calculation, solvent effects were incorporated using the PCM model in which the continuum aqueous phase is a very dilute solution so that a solute molecule is immersed in the solvent.

III. RESULT AND DISCUSSION

Geometry optimization of the host (hydrates) + guest (H_2, N_2, O_2, CO, CH_4 and NH_3) complexes were obtained from ab initio calculations by using the Gaussian-03 program package [36]. The lowest energy complexes were locally minimized at the density functional theory (DFT) level with the M05-2X functional and a 6-311++G** basis set. The resulting interacting pair structures are shown in Figure 1.

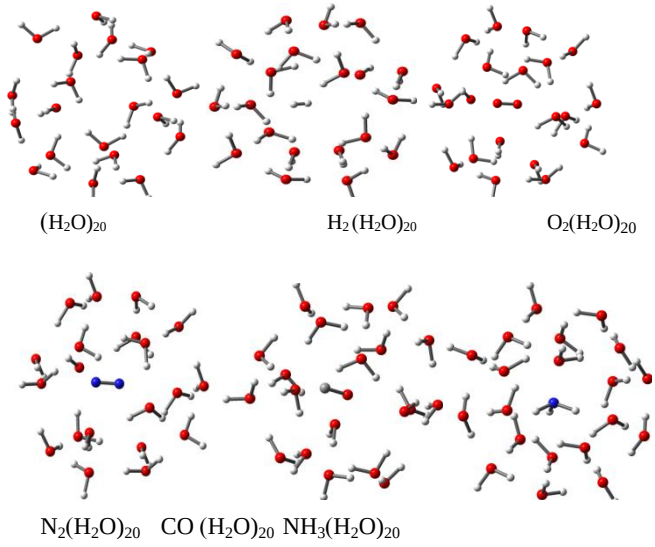

Figure 1. Optimized geometry of the dodecahedral water cage $(H_2O)_{20}$ at the M05-2X/ 6-311++G** level of theory.

Empty cage + Guest molecule ⟶ occupied cage

The geometric results computed at M05-2X functional with 6-311++G** basis set are listed in Table 1.

Complexes	$R_{G...Ow}$	$R_{Ow\cdots Ow}$
5^{12}	-	2.599
$H_2@5^{12}$	3.631	2.584
$N_2@5^{12}$	3.543	2.582
$O_2@5^{12}$	3.532	2.581
$CO@5^{12}$	3.435	2.578
$CH_4@5^{12}$	3.411	2.577
$NH_3@5^{12}$	3.391	2.512

The shortest distance between the terminal atoms of the guest molecule and the oxygen atoms of the water molecules ($R_{G\cdots Ow}$) is listed in Table 1. The distance between the the oxygen atoms of the water molecules ($R_{Ow\cdots Ow}$) is listed in Table 1. R_{G_Ow} and $R_{Ow\cdots Ow}$ comfortably used to describe the geometries (seeFig 1). R_{G_Ow} and $R_{Ow\cdots Ow}$ was employed in order to determine the strength of guest molecule interactions. It is worth mentioning that the R_{G_Ow} and $R_{Ow\cdots Ow}$ of occupied cage is greater than that of empty cage (See Table 1).The maximum and minimum value of R_{G_Ow} and $R_{Ow\cdots Ow}$ for the complexes at M05-2X method corresponds to H_2 (3.631 and 2.584 Å) and NH_3 (3.402 and 2.571 Å), respectively.

Thereby, trend of R_{G_Ow} and $R_{Ow\cdots Ow}$ is proposed as: NH_3< CH_4< CO < O_2< N_2< H_2 the values of R_{G_Ow} and $R_{Ow\cdots Ow}$ distance decrease. R_{G_Ow} and $R_{Ow\cdots Ow}$ for polar gas molecules (NH_3, CH_4, CO) are less than the unpolar gas molecules (O_2, N_2, H_2).

The excess partial molar volumes and enthalpies at infinite dilution were computed at the M05-2X/ 6-311++G** level of theory using PCM theory using default solvent parameters for water and they are given in Table 2. The computed excess partial molar volumes and enthalpies at infinite dilution were calculated from the difference between the volumes and enthalpies of solution when passing from pure liquids to their mixtures according to equation 1. An overview of computed thermochemical properties for these complexes ($V_i^{E,\infty}$ and $H_i^{E,\infty}$) are tabulated in Table 2.

Complexes	$V_i^{E,\infty}$	$H_i^{E,\infty}$	α
$H_2@5^{12}$	-18.33	-8.23	1.2
$N_2@5^{12}$	-18.11	-8.94	1.53
$O_2@5^{12}$	-17.33	-9.22	1.54
$CO@5^{12}$	-16.99	-9.87	1.76
$CH_4@5^{12}$	-15.19	-10.12	1.78
$NH_3@5^{12}$	-14.22	-10.33	1.99

As listed in Table, Host–guest interaction between hydrates and guest molecules (H_2, N_2, O_2, CO, CH_4 and NH_3) occurs which makes a negative contribution to $V_i^{E,\infty}$. Noncovalent interaction of the cage due to the presence of guest molecules was influence which decreases the volume. The analyzing the quantities at infinite dilution $V_i^{E,\infty}$, one may derive an information about of host + guest interactions. Thermodynamics studies of host + guest complexes at infinite dilution clearly show the effect of the polarizability of guest molecules in the host-guest interaction. For given mixtures the negative values of $V_i^{E,\infty}$ become larger as the polarizability of guest molecules increase.

From Table 2 we see that the excess partial molar volumes at infinite dilution $V_i^{E,\infty}$ for polar gas molecules (NH_3, O_3, CO) are more than the excess partial molar volumes at infinite dilution $V_i^{E,\infty}$ for unpolar gas molecules (H_2, N_2, O_2, CH_4). So that the maximum/minimum absolute values of $V_i^{E,\infty}$ are related to hydrate + NH_3/H_2 interaction, respectively. The absolute trend for is NH_3> CH_4> CO > O_2> N_2> H_2.

Following optimization, $H_i^{E,\infty}$ for each of the structures was evaluated at the same level of theory as that used for optimization using mentioned equation. It should be noted that when discussing the minimum energy structures for occupied cage, frequency calculations were carried out using the density functional theory (DFT) theory. enthalpy for the optimized geometries were obtained from the frequency calculations by using the harmonic oscillator and rigid rotor approximations at 298.15 K and 1 atm, calculated at the M06-2X/6-311++G** level of theory.

Computational data were determined for each host + guest complexes excess partial molar enthalpies at infinite dilution ($H_i^{E,\infty}$) and reported in Table 2. The magnitude of $H_i^{E,\infty}$ is an excellent indicator of the strength of interaction between unlike molecules. The calculated excess partial molar enthalpies at infinite dilution were negative, suggesting that trapping a variety of guest species inside the cages of clathrate hydrates is exothermic in all host + guest complexes at infinite dilution.

The excess molar enthalpies are negative for the all host + guest complexes and increase with increase in the polarizibility of the guest molecules. It indicates that the excess molar enthalpies are strongly influenced by the polarizibility of the guest molecules. In the case of hydrate +

NH_3 mixtures in water solvent, $H_i^{E,\infty}$ is affected by polarizibility of the NH_3 and consequently strengthen the interaction between host and guest. In more polar molecules, the increase in the values of $H_i^{E,\infty}$ shows the higher release of energy for guest molecules trapped. The maximum/minimum values of $H_i^{E,\infty}$ were observed for host (hydrate) + NH_3/H_2 complexes. As it can be seen, these values are depending on the polarizibility of the guest, The values of $H_i^{E,\infty}$ are in order $NH_3 > CH_4 > CO > O_2 > N_2 > H_2$.

IV. Conclusion

The present paper reports the results of computational excess partial molar volumes and enthalpies at infinite dilution for host (hydrate) + guest (H_2, N_2, O_2, CO, CH_4 and NH_3) complexes by ab initio method at the M05-2X/6-311++G** level of theory using PCM theory. This negative value of $H_i^{E,\infty}$ is consistent with exothermicity of these complexes. From an examination of the data listed in Table 4, it is clear that the values of the infinite dilution excess partial molar enthalpies of hydrate + NH_3 were more than hydrate + H_2 and have the following order: $H_2 < N_2 < O_2 < CO < CH_4 < NH_3$. It is indicated that NH_3 is more easily interact with hydrate than H_2, the polarizibility of NH_3 causes the more interaction than H_2.

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