

Investigation of Physicochemical Properties of Aggregated Models of $[\text{MIM}^+]_2[\text{C}(\text{CN})_3^-]_2$ Ionic Liquid: A Theoretical Study

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In the present work, the aggregation behavior of ion-pairs in $[\text{MIM}^+]_2[\text{C}(\text{CN})_3^-]_2$ ionic liquid was investigated. The quantum chemical calculations were carried out to determine the structural parameters, interaction energies, hydrogen bonding, physical and topological properties of the clusters formed in the ionic liquid of $[\text{MIM}^+]_2[\text{C}(\text{CN})_3^-]_2$. The solvent effect on the stability of clusters was examined. The Gibbs free energy of solvation and the Gibbs free binding energy of clusters in various solvents were calculated. The results show that with decreasing the polarity of the solvent, the tendency to the formation of aggregate increases. Also, the solvation energies of the clusters increase with decreasing the solvent's dielectric constant. The NBO analysis was performed to evaluate the charge transfer in complexes. The AIM analysis was performed in order to characterize the intermolecular interactions.

Keywords: $[\text{MIM}^+]_2[\text{C}(\text{CN})_3^-]_2$ Ionic liquid, Solvent effect, Aggregation, Interaction energy

INTRODUCTION

The use of toxic and hazardous organic solvents is one of the most important problems in the chemical industry. Therefore, there is a fundamental need to find out a replacement for the toxic solvents used in the chemical processes. The most important alternatives to toxic solvents are ionic liquids. Ionic liquids (ILs) are salts with melting points below 100 °C, which can replace toxic organic solvents in a range of well-known processes [1-3]. Ionic liquids generally consist of organic or inorganic cations and organic anions [4]. Due to their unusual properties such as low flammability, extremely low vapor pressure, high thermal and chemical stability, as well as large liquids range and wide electrochemical window, ILs have attracted a lot of attention [5-7]. These unique properties of ionic liquids have increased their application in diverse fields, such as synthesis and catalysis [8], chemical engineering [9], electrochemistry [10], pharmaceutical chemistry [11,12] and

many others. Since ILs are composed of cations and anions, therefore one ion-pair can be considered as the fundamental unit for the IL. Most cations of ILs, such as imidazolium and pyrrolidinium, with long-chain, containing a hydrophilic head and hydrophobic tails, possess an inherent amphiphilic nature. ILs due to the amphiphilic nature of their cations can form self-assemble structures and exhibit cluster/ aggregate behaviors in slightly polar solvents [13]. The electrostatic interactions in ILs lead to the formation of ion-pairs and clusters [14]. In the past few years, some researchers have shown that ionic liquids have the ability to form different aggregates/clusters such as micelles, vesicles and liquid crystals in aqueous and non-aqueous solutions [15-17]. Cluster science is an interesting field in materials, as clusters are often envisaged as building blocks for microstructures materials. The microstructure of ionic liquids has gained much attention because of their relation to the physicochemical properties and behavior of ILs. The existence of microstructures or clusters in ILs is an important characteristic of many ILs and provides important information to better understand IL applications in various

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fields. The formation of the cluster in ILs plays a key role in IL-involving reactions and processes. In recent years, clusters/aggregates formation in ionic liquids has been reported by theoretical and experimental methods [13]. Tokuda *et al.* with measurement of viscosity and the electrical conductivity of a series of ILs, reported the existence of the clustering of ions in bulk ILs [18]. For the first time, cluster formation in ILs was reported with molecular dynamics (MD) study and provided an in-depth understanding of the behavior of liquids at the molecular level [19]. Formation of the cluster in water, organic solvents, and liquid metals have been investigated by spectroscopic techniques as well as theoretical calculations [20,21]. The self-aggregation behavior of ILs can affect processes such as the synthesis and purification of ILs, the extractions of products from IL-containing systems and the solvation properties of the ILs [22]. Many studies have shown that ionic conductivities of ILs can be changed by their aggregation [23-25]. Findings show that the cluster formation takes place in most ILs, especially in ionic liquids containing 1-alkyl-3-methylimidazolium cation. Wang *et al.* investigated the aggregation behaviors of [C₈mim]Br, 1-octyl-4-methyl pyridinium bromide (4-m-[C₈pyr]-Br), and 1-methyl-1-octyl pyrrolidinium ([C₈mpyr]Br). They found that the hydrophobicity of the cations plays a significant role in the aggregation of these ILs [26]. The aggregation of [C₄mim][BF₄] in water, methanol, 2-propanol, and ethyl acetate by electrospray ionization mass spectrometry was studied by Dorbritz *et al.* They explored that with increasing polarity of the solvent and decreasing concentration of the IL, the size of the clusters formed decrease [27]. Chaban and Fileti investigated the correlation between viscosity and ionic liquid clusters in aqueous solutions [28]. Molecular dynamics studies were performed on the structure and nature of the aggregates in ionic liquids containing amino-acid anions [29]. The thermostability, structural parameters and viscoelasticity for the various clusters of 1-butyl-3-methyl imidazolium dodecyl sulfonate ([C₄mim][C₁₂H₂₅SO₃]) were studied by Tian *et al.* [30]. The physicochemical properties of clusters of [MIM⁺][N(CN)₂] ionic liquid been have studied by Roohi *et al.* [31]. Information on the physicochemical properties of clusters is limited despite many studies performed on the aggregation behavior of ILs. Therefore, designing new anions, cations,

and their combinations may develop new ionic liquids. In this work, the clusters of [MIM⁺]₂[C(CN)₃]⁻₂ ionic liquid are investigated. The aims of this study are 1- finding clusters formed from the interaction between 2MIM⁺ and 2C(CN)₃⁻ ions, 2- calculation of binding energy and geometrical parameters, 3- investigation of the physicochemical properties of clusters in the gas and solution phases, and 4- characterization of the nature of intermolecular interactions in clusters.

Computational Methods

All structures were optimized using the B3LYP [32,33], MP2 [34] M052X [35] and M062X [36] methods applying 6-311++G(2d,2p) basis set [37]. Frequency calculations were performed to characterize the stationary points and calculation of zero-point energy at all levels of theory. The counterpoise procedure was used to correct basis set superposition error (BSSE) in the calculation of binding energies [38]. All calculations were performed using Games [39] and the Gaussian program [40]. The NBO and AIM analyses were carried out at the MP2/6-311++G(2d,2p) level of theory [41,42]. The solvent effect on the aggregate stability was examined at the MP2/6-311++G(2d,2p) level of theory by applying the polarizable continuum model (PCM) [43]. The Gibbs free energy of solvation (ΔG_{solv}^0) for the solubility of the solute species in a solvent and the change in Gibbs free energy of solvation ($\Delta\Delta G_{\text{solv}}^0$) were calculated according to the relation of $\Delta G_{\text{solv}}^0 = \Delta G_{\text{ele}}^0 + \Delta G_{\text{nonele}}^0$ and $\Delta\Delta G_{\text{solv}}^0 = \Delta G_{\text{solv,cluster}}^0 - (2\Delta G_{\text{solv, ion-pair}}^0)$, respectively. The interaction Gibbs free energy of clusters in solution (ΔG_{sln}^0) was calculated according to the relation of $\Delta G_{\text{sln}}^0 = \Delta\Delta G_{\text{solv}}^0 + \Delta G_{\text{g}}^0$.

RESULTS AND DISCUSSION

Energies and Geometries

The quantum chemical calculations were performed in [MIM⁺][C(CN)₃]⁻ ionic liquid where two cations and two anions intermittently and simultaneously interact with each other and form a ring cluster. Totally, four stable clusters were found on the potential energy surfaces. The molecular structures of clusters are shown in Fig. 1. In all clusters, anions are located between cations and are formed cyclic systems with four hydrogen bonds, so that, the N-H and

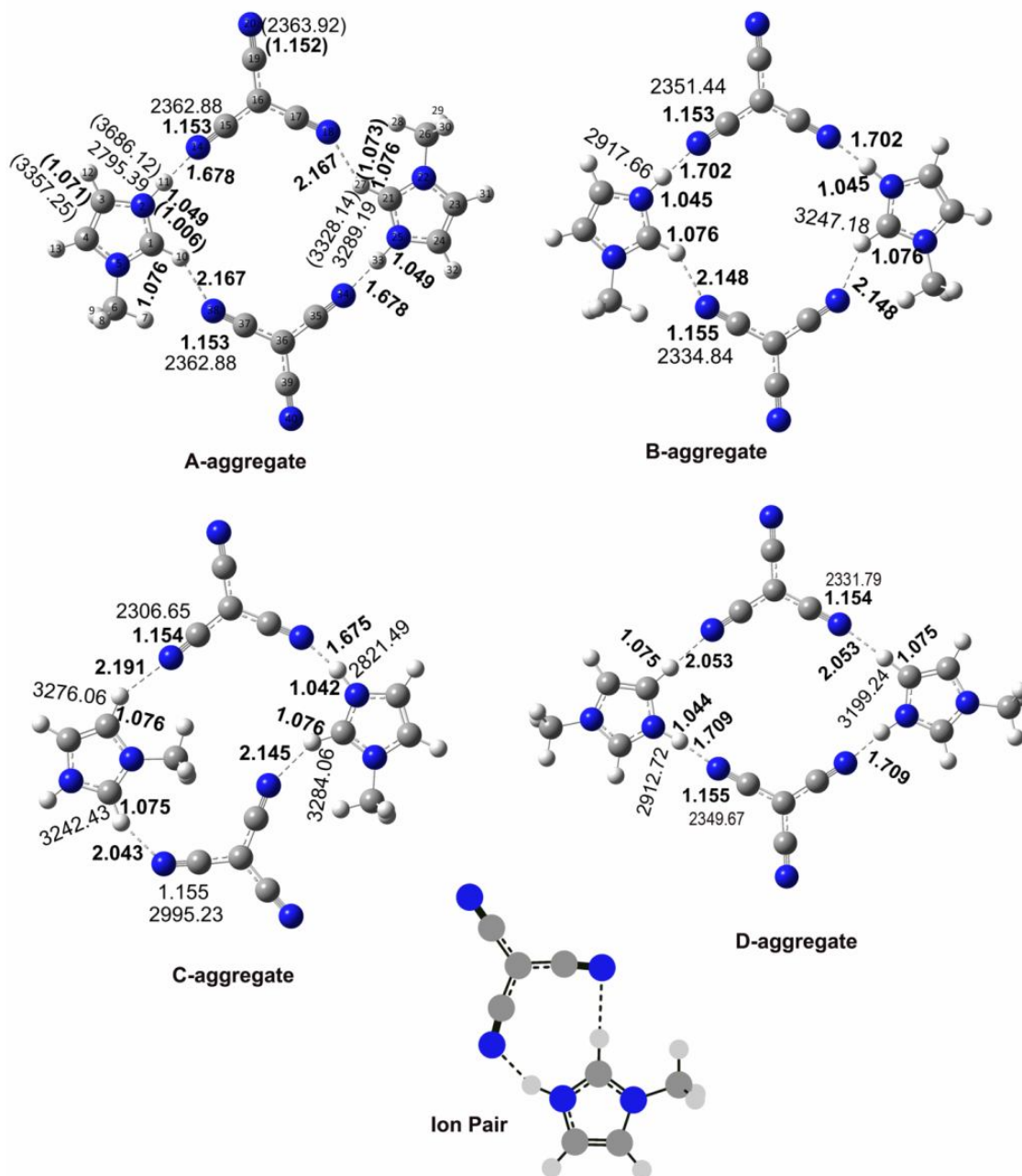


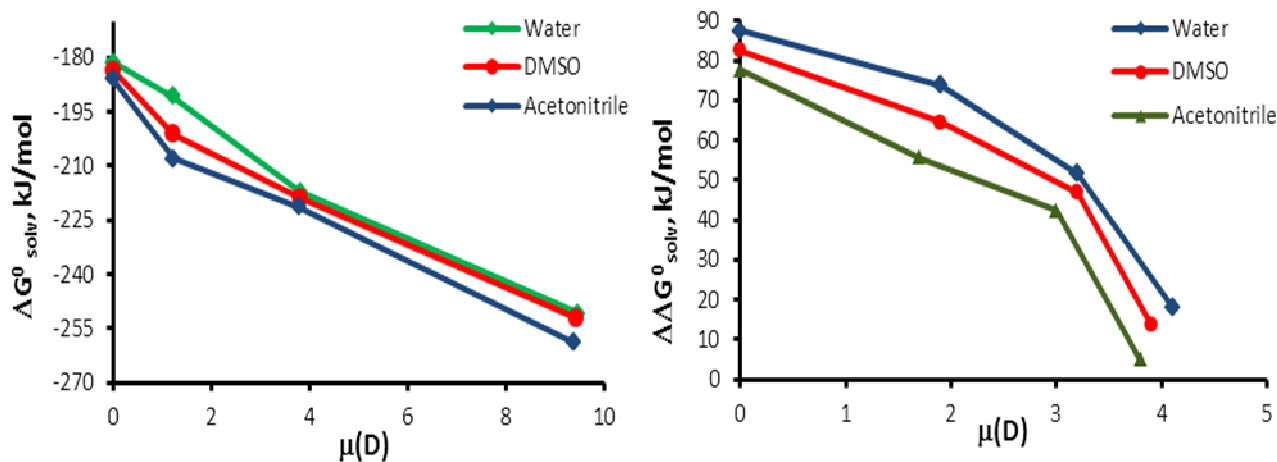
Fig. 1. Optimized bond lengths (in Å) and N-H and C-H bond vibrational frequencies (cm^{-1}) for cation and anion (in the parentheses) and A-D clusters at the MP2/6-311++G(2d,2p) level of theory.

C-H bonds of cations and C-N bonds of anions are involved in interactions. Therefore, in A, B and D clusters, two NH...N and two CH...N hydrogen bonds and in C cluster, one NH...N and three CH...N hydrogen bonds were observed.

In A, B and C clusters, methyl groups of cations interact with anions. Therefore, these additional interactions can be effective in the stability of A, B, and C clusters compared to D cluster. In A-D clusters, N-H and C-H bonds of cations act as a proton donor and N atoms of anions act as a

Table 1. The Interaction Energies (kJ mol⁻¹) for A-D Clusters at Different Levels of Theory

Cluster	Method	BSSE	$\Delta E_{\text{elec}}^{\text{Bsse}}$	ΔE^{oBsse}	ΔG^{oBsse}	ΔH^{oBsse}
A	B3lyp/6-311++G(2d,2p)	2.10	-107.30	-104.25	-86.44	-84.34
B		1.86	-106.22	-102.56	-68.50	-66.64
C		1.53	-62.38	-59.23	-35.04	-33.51
D		1.72	-53.14	-51.49	-33.91	-32.19
A	M05-2X/6-311++G(2d,2p)	1.80	-101.60	-98.22	-57.38	-55.58
B		2.05	-100.46	-94.86	-67.64	-65.60
C		1.80	-67.02	-61.64	-22.29	-20.48
D		1.90	-39.32	-35.88	-8.33	-6.44
A	M06-2X/6-311++G(2d,2p)	2.16	-102.14	-92.94	-56.22	-54.06
B		2.00	-101.09	-90.10	-57.71	-55.71
C		2.16	-67.37	-56.24	-16.80	-14.64
D		1.85	-39.47	-31.56	-8.81	-6.95
A	MP2/6-311++G(2d,2p)	2.65	-101.53	-90.29	-42.37	-28.13
B		2.18	-100.70	-87.66	-45.67	-33.49
C		1.78	-66.14	-52.97	-4.93	5.85
D		2.56	-39.69	-31.74	1.68	13.58

**Fig. 2.** Relationship between $\Delta G^{\circ}_{\text{solv}}$ and $\Delta\Delta G^{\circ}_{\text{solv}}$ of clusters with the dipole moment of the solute in the solution.

proton acceptor. The structural parameters of clusters at the MP2/6-311++G(2d,2p) level of theory are reported in Fig. 1. As can be seen, in all clusters, the N...H-N hydrogen bonds are shorter than the N...H-C hydrogen bonds, thus, the N...H-N interactions expected to be stronger than N...H-C interactions. The calculated vibrational frequencies at the MP2/6-311++G(2d,2p) level of theory are reported in Fig. 1. In all clusters, the computations predict a red-shift with respect to the isolated ions in the vibrational frequencies of C-H and N-H bonds involved in the interaction. These results are in agreement with the increased length of these bonds. In all clusters, the value of red-shift and increasing the length of the N-H bonds involved in the interaction are more than those in C-H bonds. Also, in A and B clusters, the value of red-shift and the increase of the N-H and C-H bond lengths involved in the interaction are more than those in other clusters. Therefore, it is expected that the N...H-N interactions to be stronger than C...H-N interactions. Also, in A and B clusters, N...H-N and C...H-N interactions expected to be stronger than those in C and D ones. Our results also show a red-shift in the vibrational frequency of the C≡N bonds of the anions in clusters. The calculated values of electronic interaction energy (ΔE_{elec}) for all of the studied complexes, including BSSE ($\Delta E_{\text{elec}}^{\text{BSSE}}$) and zero-point energy (ZPE) corrections (ΔE^0), or both BSSE and ZPE corrections (ΔE^{0BSSE}), at various levels of theory, are reported in Table 1.

Based on the previous work, the ion-pair structure is more stable than the separate ions in the gas phase [44]. Thus, in this work, the values of electronic interaction energy (ΔE_{elec}) can be calculated according to the formula $\Delta E_{\text{elec}} = \Delta E_{\text{elec, cluster}} - (2\Delta E_{\text{elec, ion-pair}})$. The relative stability of clusters decreases in the order $A > B > C > D$. In addition, by employing ZPE and BSSE corrections, the order of clusters stability did not change. It seems that the orientation of methyl groups of cations plays an important role in the stability of clusters. Compared with the previous work, the formation of A-D complexes is more favorable than that of A-D cluster formation in the gas phase. In this work, we have investigated the Gibbs free energy of solvation in different solvents and the Gibbs free binding energy of clusters in the gas phase at the MP2/6-311++G

(2d,2p) level of theory and data are reported in Table 2.

The solubility of a solute in a solvent is determined by the Gibbs free energy of solvation (ΔG_{solv}^0). The results of ΔG_{solv}^0 show that the process of dissolution is spontaneous. From Table 2, the ΔG_{solv}^0 values of all clusters in all solvents are negative and decrease in the order of $D > C > B > A$. There is a correlation between ΔG_{solv}^0 and $\Delta\Delta G_{\text{solv}}^0$ of complexes with the dipole moment of the solute in the solution, which is shown in Fig. 2. In all three solvents, the values of ΔG_{solv}^0 and $\Delta\Delta G_{\text{solv}}^0$ decrease as the dipole moment of the complexes increases. Therefore, the ΔG_{solv}^0 value is bigger for solute with higher polarity.

The correlation between $\Delta\Delta G_{\text{solv}}^0$ and ΔG_{solv}^0 of complexes with the dielectric constant of the solvent are shown in Fig. 3. Both $\Delta\Delta G_{\text{solv}}^0$ and ΔG_{solv}^0 values decrease as the dielectric constant of the solvent increases.

The values of ΔG_{sh}^0 show that the formation of clusters in the solution phase is not a spontaneous process. These values in A-D clusters decrease with decreasing dielectric constant of the solvent. Therefore, it can be said that with decreasing the polarity of the solvent the tendency to the formation of aggregate increases. Comparing the values of $\Delta\Delta G_{\text{solv}}^0$ and ΔG_{sh}^0 of aggregates with the ion-pair complex reveals that there is a tendency for the formation of aggregates in the solution phase. The interaction energies for clusters are calculated at the MP2/6-311++G(2d,2p) level of theory in three different solvents, and the results are reported in Table 2. In the solution phase, the calculated interaction energies (ΔE_{sh}) for clusters are lower than those in the gas phase and reduce with increasing the solvent's dielectric constant. On the other hand, the solvation energies of clusters decrease smoothly with decreasing the solvent's dielectric constant. Therefore, the tendency of ions to form the clusters decreases with increasing the solvent's dielectric constant. Also, in the presence of solvents, the stability of the clusters decreases with respect to the separate ions. The relationship between ΔE_{sh} and E_{solv} with the dielectric constant of the solvent is shown in Fig. 4.

The ΔE_{sh} values in all solvents decrease in the order of $A > B > D > C > \text{IP}$. Thus, compared with our previous work [44], the stability of the clusters in the presence of solvent is greater than that in the ion-pair forms of the ionic liquid.

Table 2. The Electrostatic ($\Delta G^{\circ}_{\text{ele}}$) and Non-electrostatic ($\Delta G^{\circ}_{\text{nonele}}$) Contributions to the Gibbs Free Energy of Solvation ($\Delta G^{\circ}_{\text{solv}}$), the Change in Gibbs Free Energy of Solvation ($\Delta\Delta G^{\circ}_{\text{solv}}$), the Gibbs Free Binding Energy of Aggregates in the Gas Phase ($\Delta G^{\circ}_{\text{g}}$), the Gibbs Free Binding Energy of Clusters in Solution ($\Delta G^{\circ}_{\text{sln}}$), the Interaction Energy in Solution (ΔE_{sln}), Solvation Energy E_{solv} (in kJ mol^{-1}), and Dipole Moment of the Clusters in Gas Phase (μ_{g}) and Solution (μ_{sln}) (in D). The Gibbs Free Binding Energies are in kJ mol^{-1}

	$\Delta G^{\circ}_{\text{ele}}$	$\Delta G^{\circ}_{\text{nonele}}$	$\Delta G^{\circ}_{\text{solv}}$	$\Delta\Delta G^{\circ}_{\text{solv}}$	$\Delta G^{\circ}_{\text{g}}$	$\Delta G^{\circ}_{\text{sln}}$	ΔE_{sln}	E_{solv}	μ (g)	M (Sln)
Water										
A	-271.37	90.08	-181.29	87.57	-57.38	30.19	-35.57	-126.00	0.00	0.00
B	-280.33	89.54	-190.79	78.07	-67.64	10.43	-30.42	-126.74	0.07	1.22
C	-307.78	90.58	-217.19	51.67	-22.29	29.38	-20.03	-143.03	2.39	3.81
D	-341.87	91.13	-250.75	18.12	-8.33	9.78	-24.30	-178.91	7.48	9.47
Anion	-239.62	32.05	-207.57					-218.60		
Cation	-283.42	19.00	-264.43					-198.26		
IP	-178.95	44.52	-134.43	337.57	-305.15	32.42	-5.07	-97.91	16.02	18.83
Dmso										
	0.00									
A	-207.19	23.81	-183.38	284.39	-57.38	227.00	-38.47	-124.39	0.00	0.00
B	-225.31	24.06	-201.25	266.52	-67.64	198.88	-36.32	-125.13	0.07	1.22
C	-243.89	24.94	-218.95	248.82	-22.29	226.53	-25.70	-141.20	2.39	3.80
D	-278.11	26.02	-252.09	215.69	-8.33	207.35	-28.57	-176.68	7.48	9.44
Anion	-227.82	22.09	-205.73					-216.68		
Cation	-257.99	-4.06	-262.04					-196.51		
IP	-147.74	14.81	-132.93	334.85	-305.15	29.70	-5.64	-96.66	16.02	18.81
Acetonitrile										
	0.00									
A	-188.57	2.59	-185.98	278.53	-57.38	221.15	-41.15	-123.15	0.00	0.00
B	-210.71	2.72	-207.99	256.52	-67.64	188.88	-40.00	-123.89	0.07	1.22
C	-225.22	3.97	-221.25	243.26	-22.29	220.97	-27.22	-139.79	2.39	3.78
D	-263.51	4.73	-258.78	205.73	-8.33	197.39	-30.78	-174.96	7.48	9.40
Anion	-219.33	15.02	-204.30					-215.19		
Cation	-251.17	-9.04	-260.20					-195.158		
IP	-135.73	3.93	-131.80	332.71	-305.15	27.56	-5.83	-95.70	16.02	18.78

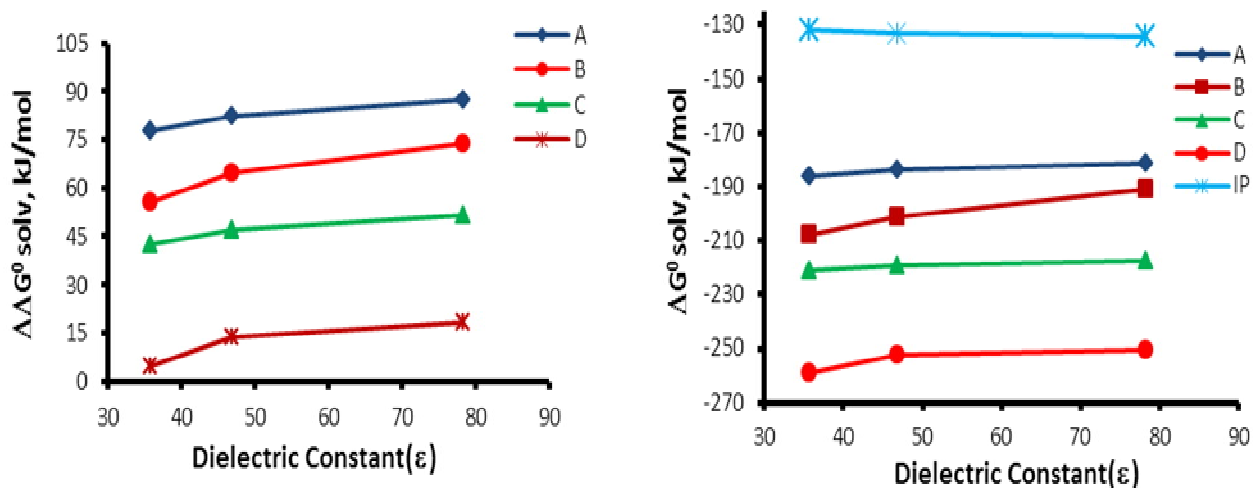


Fig. 3. Relationship between $\Delta G^{\circ}_{\text{solv}}$ and $\Delta\Delta G^{\circ}_{\text{solv}}$ of clusters with the dielectric constant of the solvent.

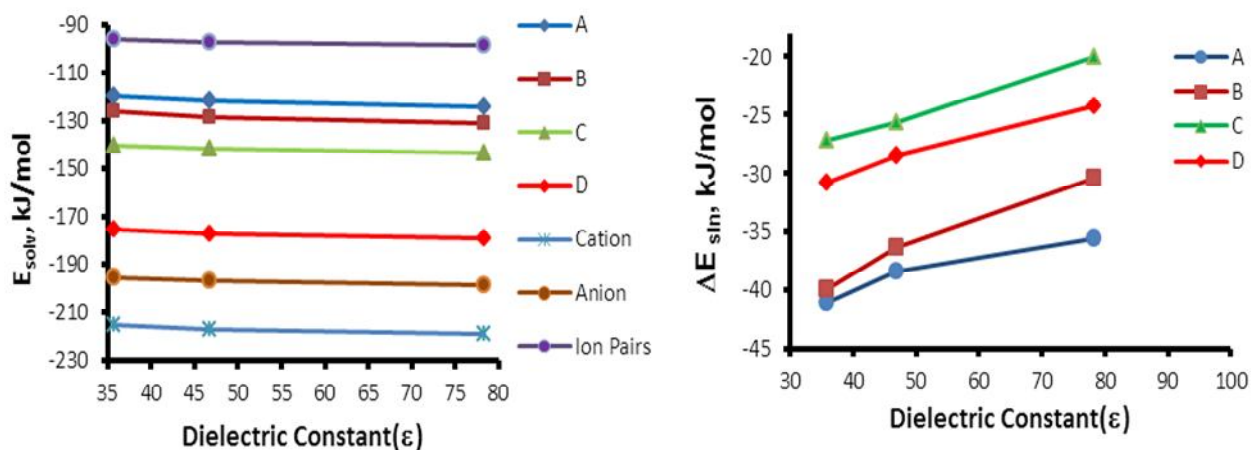


Fig. 4. Relationship between ΔE_{solv} and E_{solv} with the dielectric constant (ϵ) of the solvent

NBO and AIM Analyses

In the formation of hydrogen bonds, a certain amount of electronic charge transfer occurs from the proton acceptor to the proton donor molecule. These electronic charge transfers are investigated using the NBO analysis. The results of the NBO analysis, including CT energy, natural charge and the occupancy of NBOs at the MP2/6-311++G(2d,2p) level of theory are given in Table S1 (See supplementary material). In free cation, the charge of H atoms in N-H and C-H bonds is positive and increases in clusters. Whereas, the positive charge of C atom of C-H

bonds and the negative charge of N atom of N-H bonds decreases and increases in clusters, respectively. Upon clusters formation, the negative charge of the central C atom and the positive charge of other C atoms of anion decreases and increases, respectively. The negative charge of N atoms involved in the interaction, increases in clusters. These changes of electronic charges on atoms cause a charge transfer from anions to cations in clusters. Based on the NBO results, in all clusters, the charge transfer takes place from anions to cations that cause decreases in the positive charge of the cations. The amount of the charge transfer

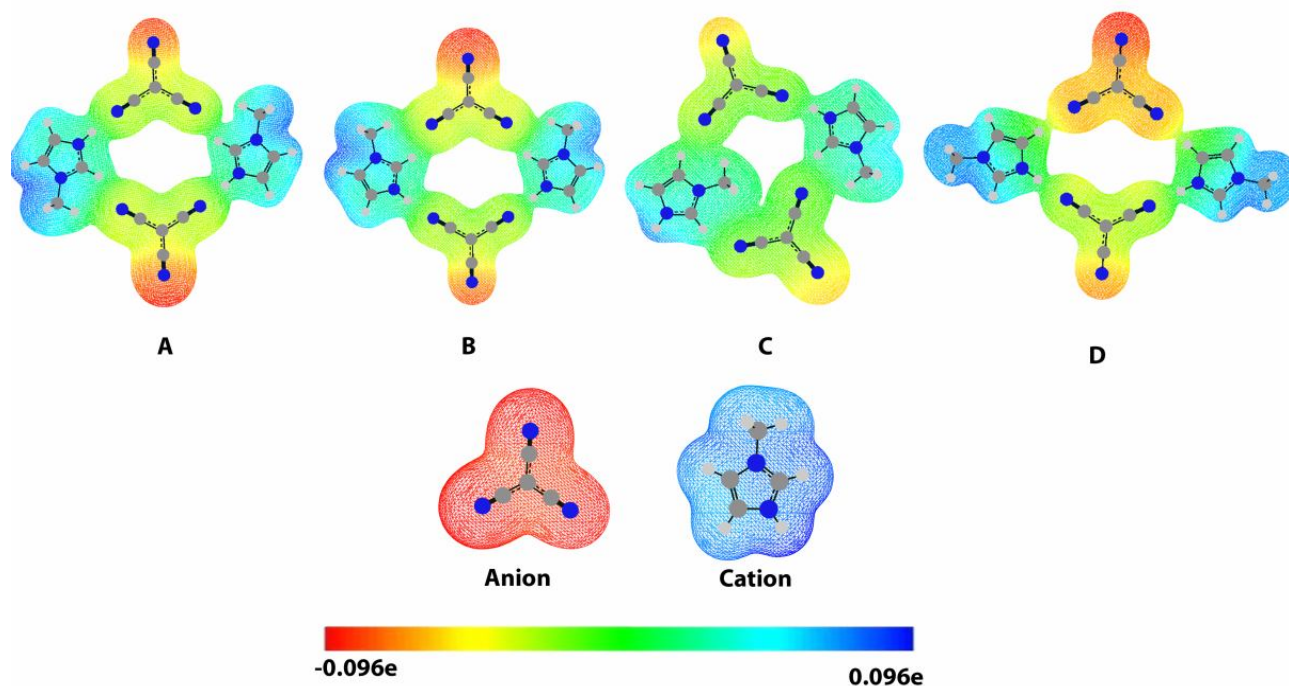


Fig. 5. Molecular electrostatic potentials calculated at the MP2/6-311++G(2d,2p) level and mapped onto the 0.0004 electron density isosurface for the cation, anion and for A-D clusters.

decreases on going from A to D clusters. The $LP(N)_{\text{Anion}} \rightarrow \sigma^*(N-H)$ and $LP(N)_{\text{Anion}} \rightarrow \sigma^*(C-H)$ donor-acceptor interactions are the most important interactions in these clusters. The sum of the charge transfer energy $E^{(2)}$ corresponding to these interactions in A-D clusters is 454.93, 425.18, 321.88 and 302.25 kJ mol^{-1} , respectively. In A-D clusters, the charge transfer energy corresponding to the $LP(N) \rightarrow \sigma^*(N-H)$ interaction is higher than that in the $LP(N) \rightarrow \sigma^*(C-H)$ interaction, indicating the $N \cdots H-N$ interaction is stronger than the $N \cdots H-C$ interaction. The NBO results show that the occupation number of the antibonding orbitals of N-H, C-H and $C \equiv N$ bonds increase upon the formation of clusters. An increase of the electron density is accompanied by the bond elongation in these orbitals leading to the weakening of N-H, C-H and $C \equiv N$ bonds.

The quantum theory of atoms in molecules (QTAIM) is a useful tool to characterize the chemical bonds. To investigate the nature of interactions in clusters, analysis of atoms in molecules was performed at MP2/6-311++G(2d,2p) level of theory. The molecular

graphs, including the critical points and bond paths for clusters, are shown in Fig. S1 (See supplementary material). For all clusters, the molecular graphs represent four additional critical points in the intermolecular region. The values of electron density ($\rho(r)$), Laplacian of the electron density ($\nabla^2\rho(r)$) and total energy density ($H(r)$) at the bond critical points (BCPs) are given in Table S2 (see supplementary material). There is a relation between the value of $\rho(r)$ at the $N \cdots HC$ and $N \cdots HN$ BCPs with bonding distances. The values of $\rho(r)$ at $N \cdots HN$ bond critical points are greater than those at $N \cdots HC$ bond critical points. Thus, $N \cdots HN$ hydrogen bonds are shorter and stronger than $N \cdots HC$. It is predicted that in all clusters, $N \cdots HN$ interactions are stronger than $N \cdots HC$ ones. Based on Table S2 (see supplementary material), $\rho(r)$ at N-H and C-H bond critical points decreases upon the formation of clusters that are in agreement with increasing the corresponding bond distances. In all clusters, the values of $\nabla^2\rho(r)$ and $H(r)$ in $N \cdots HN$ hydrogen bonds are positive and negative, respectively, whereas, these values are positive in $N \cdots HC$ hydrogen bonds. These results indicated that $N \cdots HN$ and

N...HC interactions have a partial covalent and an electrostatic nature, respectively. Therefore, it can be said that N...HN interactions are stronger than N...HC ones.

Molecular Electrostatic Potential Analysis

Molecular electrical potential (MEP) maps are three-dimensional diagrams of molecules providing some information about the charge distribution of a molecule. Figure 5 shows MEPs calculated at MP2/6-311++G(2d,2p) level of theory for cation, anion and A-D clusters. In these diagrams, the red and blue regions correspond to the regions with the greatest and lowest electron density, respectively. As can be seen in Fig. 5, in isolated ions, the blue color coincides with the molecular region having the positive electrostatic potential, while the red color coincides with the molecular region having the negative electrostatic potential. Upon the clusters formation, the observed positive regions in cations interact with any negative regions of anions. As a result of these interactions, the positive charges on cations are distributed on the methyl groups and C-H and N-H bonds of rings. Thus, a combination of red, green, blue, and yellow colors can be seen in clusters.

CONCLUSIONS

In this work, the quantum chemical calculations were used to study the aggregation behavior of $[\text{MIM}^+]_2[\text{C}(\text{CN})_3^-]_2$ ionic liquid in the gas and solution phases. Two $[\text{C}(\text{CN})_3^-]$ anions combined with two $[\text{MIM}^+]$ cations result in the formation of clusters with four intermolecular hydrogen bonds. The results show that the C-H...N interactions are weak compared to the N-H...N interactions observed between cations and anions. In the solution phase, the tendency to aggregation decreases with increasing the polarity of solvent. It is estimated that the association of ions to form the aggregates decreases with increasing the solvent's dielectric constant. In comparison with the previous study [44], ions have more tendency for aggregation in the solution phase. It seems that the physicochemical properties of clusters are in a good agreement with previously reported results of $[\text{MIM}^+][\text{C}(\text{CN})_3^-]$ ionic liquid. The NBO results show that the charge transfer (CT) takes place from anions $\text{C}(\text{CN})_3^-$ to cations MIM upon complexation. Based on the AIM results,

N...HN and N...HC interactions have a partial covalent and an electrostatic nature, respectively.

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