

Theoretical Study on Structures and Energetics of Small Water Clusters

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A study of small water clusters composed of two to seven molecules has been performed by using the revised empirical potential function for conformational analysis (REPFCA). Various structures of clusters have been investigated and the relative probability of cluster per molecule is discussed. In general, cyclic structures of water clusters are more favorable than open structures. It is found that cyclic pentamer is the most favorable unit structure in the water cluster.

Introduction

Liquid water continues to be the subject of intense research effort because of its importance in biological, chemical, and physical systems as well as its great theoretical importance as an example of liquid with strong noncentral intermolecular forces.

If clusters exist in liquid water, what's the optimum number of molecules and what's the structure of cluster? To investigate answers of these problems, at first, the calculation for water dimer is carried out, and then those for large clusters containing three to seven water molecules are performed. For each cluster, the possible configurations are considered and the favorable configurations are chosen by minimizing the total interaction energies of clusters. To check the further validity of the used potential, the result for water dimer is compared with experimental data.

Recently, we have shown¹ that a newly proposed empirical diatomic potential is adequate to account for the O-H...O hydrogen bonds such as water, methanol, acetic acid and formic acid dimers. Since the previous work is incomplete to describe the hydrogen bonding in water, we have revised this potential and examined its validity.

To investigate the relative populations of water clusters, the relative probability of cluster per molecule is calculated and discussed.

Methods

The total potential function consists of three contributions such as electrostatic, polarization and nonbonded terms², and an additional hydrogen-bond potential.¹

$$E_{\text{tot}} = \sum_{i,j \neq hb} \sum_{i,j} (E_{e1} + E_{\text{pol}} + E_{nb}) + \sum_{hb} E_{hb} \quad (1)$$

where the summations over i and j in the first term cover all the atoms except hydrogen-bonded atoms and the summation in the second term runs over hydrogen-bonded pairs.

The electrostatic energy is given by

$$E_{e1} = \sum_{i,j} q_i q_j r_{ij}^{-1} \epsilon^{-1} \quad (2)$$

where r_{ij} is the distance between atoms i and j , q_i and q_j are the net charges of atoms i and j , respectively, and ϵ is the dielectric constant and is taken to be unity.

The polarization energy is obtained as a sum of atomic

contributions,

$$E_{\text{pol}} = -1/2 \sum_i \alpha_i (E_i)^2 \quad (3)$$

where E_i is the electric field at atom i due to the interacting molecule and α_i is the atomic static polarizability of atom i taken from Kang and Jhon.³

The nonbonded energy is given by³

$$E_{nb} = -K_6(i, j) / z_{ij}^6 (1 - 0.5/z_{ij}^6) \quad (4)$$

where $K_6(i, j) = C_6(i, j) / r_{ij}^{m_6}$ (5)

and $z_{ij} = r_{ij} / r_{ij}^*$ (6)

Here, r_{ij}^* is the sum of van der Waals radii of atoms i and j , and $C_6(i, j)$ is the dispersion coefficient of atoms i and j .

The hydrogen-bonding potential is

$$E_{hb} = E_{hb}^0(r) \cdot A(\phi) \quad (7)$$

where E_{hb}^0 represents hydrogen-bonding energy for the linear H...O-H system and $A(\phi)$ denotes the attenuating factor for the hydrogen bond. E_{hb}^0 is given by¹

$$E_{hb}^0 = D_e [1 - (r/r_e)^n \cdot e^{-a(r/r_e - 1)}]^2 - D_e \quad (8)$$

where D_e is the dissociation energy for hydrogen-bonded pair, r is the hydrogen-bonding distance, r_e is its equilibrium value, and parameter n and a have the following relationship.

$$a = n + \Delta^{1/2} \quad (9)$$

where Δ means Sutherland parameter.⁴ Since there are no available experimental data for the parameters, we assume the values of D_e , r_e , a and n to be 34.416 kcal/mol, 1.86 Å, 2.07 and 0.01, respectively.

Attenuating factor $A(\phi)$ is ascribed to the decreasing contribution of charge transfer as the hydrogen bond becomes bent, *i.e.*,

$$A(\phi) = b(\cos^2\phi - 1) + 1 \quad (10)$$

where ϕ is the bent angle of hydrogen bond and constant b is taken to be 0.456. When ϕ is less than 155° or hydrogen-bonding distance is longer than 2.37 Å, the two atoms are considered not to form a hydrogen bonding.

The geometry of water molecule is taken from the experimental values,⁵ *i.e.*, $r(\text{O-H}) = 0.9572 \text{ \AA}$ and $\angle \text{HOH} = 104.52^\circ$. By using these geometric data and experimental dipole moment, we obtain net charges of q_H and q_O . Energy minimiza-

tion is carried out using Quasi-Newton method developed by Fletcher⁶ with a convergence criterion of 0.001 kcal/mole. The minimization step lengths are 0.02 Å for distances and 0.2 degree for all angles. The number of iterations is limited to 100 iterations.

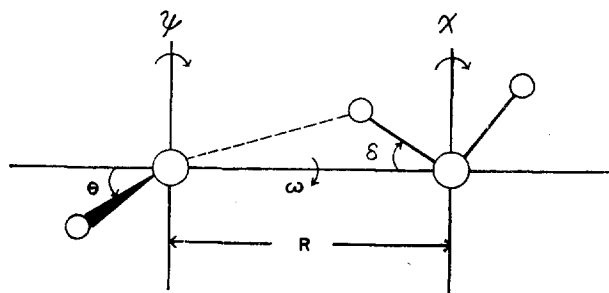


Figure 1. Geometrical parameters for dimer structure. The large and small circles represent oxygen and hydrogen atoms, respectively.

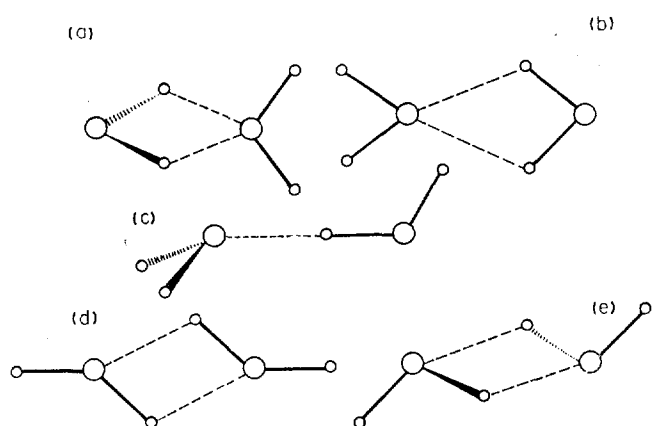


Figure 2. The structures of dimer; (a) bifurcated, (b) planar bifurcated, (c) linear, (d) planar cyclic, and (e) closed.

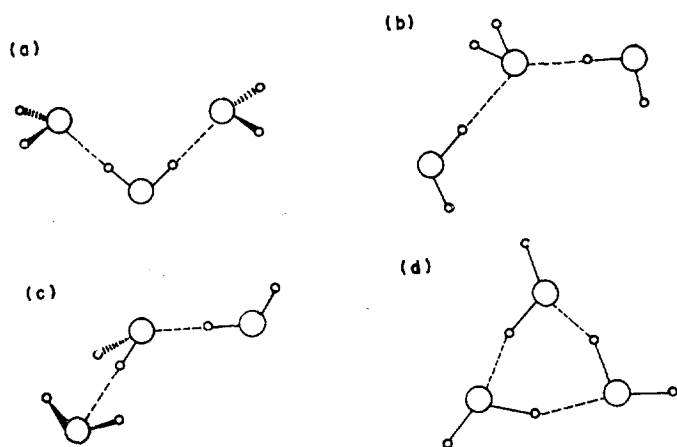


Figure 3. The structures of trimer; (a) double donor, (b) double acceptor, (c) sequential, and (d) cyclic.

Results and Discussion

1. Dimer. Several studies for water dimer have been done by using empirical and molecular orbital methods. Using molecular beam microwave spectroscopy, Dyke and Muentzer⁷ have published an experimental structure of the dimer. Measuring thermal conductivity, Curtiss and Blander⁸ have found an experimental interaction energy for the water dimer.

Geometrical parameters for water dimer structure are shown in Figure 1, where R the distance between two oxygen atoms, θ is the angle between the molecular plane and inter-oxygen axis, δ measures the inclination of OH bond of another molecule from inter-oxygen axis, and ψ and χ are the rotational angles about the axes perpendicular to oxygen-oxygen axis.

The typical structures are shown in Figure 2 and the results for dimers are given in Table 1. The linear structure is found to be the most stable one, which agrees well with other theoretical works and experimental results. The calculated geometry and physical quantities such as dimerization energy, average moment of inertia, magnitude of dipole moment and vibrational frequency of hydrogen bond are compared with other results in Table 2, which show good agreement with experimental data.

2. Trimer. While *ab initio* calculations^{16,18} have been performed to determine only the relative stability of open and cyclic water trimers, an overall optimization on the twelve-dimensional trimer potential energy surface has been carried out by using empirical potentials. Kistenmacher *et al.*¹⁹ and Scheraga *et al.*⁹ have shown that there is only one stable cyclic trimer on the twelve-dimensional potential-energy surface, and that open structures have no minimum energy.

The structures of trimers considered here are of three open types and a cyclic one, which are shown in Figure 3. Cyclic trimer is found to be the most stable configuration and the results for trimers are given in Table 3. Our REPFCA cyclic trimer has more or less longer inter-oxygen distance, nearly the same bent angles of hydrogen bond, and a slightly higher energy compared with EPEN cyclic trimer of Scheraga group.⁹ But our results for cyclic trimers are similar to the results of Clementi group¹⁹ except inter-oxygen distances. By comparing our results for open trimers with others,^{16,20,21} it is found that there are similar tendencies in interaction energies according to the geometries although the relative energies are different.

3. Tetramer. The results for tetramer obtained by optimizing the *ab initio* potential function^{16,18} revealed that cyclic

TABLE 1: Results of Dimers^a

Structure ^b	R	θ	δ	ψ	χ	ω	E_{tot}^c
Bifurcated (C_{2v})	2.78	180.	128.	0.	0.	0.	-4.19
Planar bifurcated (C_{2v})	2.78	0.	0.	0.	0.	52.	-3.90
Planar cyclic (C_{2h})	2.78	180.	0.	97.74	60.	90.	-3.46
Closed (S_2)	2.74	90.	37.7	128.3	38.3	0.	-3.61
Linear (C_1)	2.98	39.1	0.	0.	0.	0.	-5.44

^a Geometrical parameters as defined in Figure 1. ^b The structures are shown in Figure 2. ^c Units in kcal/mole.

TABLE 2: Comparison of Linear Dimer with Others

Potential	E_{tot}^a	R	θ	δ	I_{aver}^b	$ \mu ^c$	ν^d
This work	-5.44	2.98	39.1	0.0	83.08	2.47	150.4
EPEN ^e	-5.44	2.88	61.9	2.8	76.80	2.35	168.
SS ^f	-5.76	2.85	79.9	8.7	74.50	1.73	183.
AFHF ^g	-4.58	3.00	38.0	2.4	84.34	2.89	161.
ST2 ^h	-6.84	2.85	51.8	-1.1	76.05	2.72	213.
BNS ⁱ	-6.89	2.76	54.7	0.0	71.34	2.63	185.
WB ^j	-5.06	2.75	48.0	0.9	71.03	2.66	366.
<i>ab initio</i> DMP ^k	-6.09	2.73	58.0	0.0			
MCY I ^l	-5.72	2.987	32.4	2.9			166.9
MCY II ^l	-5.87	2.872	37.6	4.1			182.7
Expl. ^m	-5.44 ⁿ	2.98	58(6)	1(6)	82.06	2.60	150.

^a Units in kcal/mole. ^b Average principle moment of inertia, units in amu. Å.² ^c Magnitude of dipole moment, units in D. ^d vibrational frequency of H...O, units in cm⁻¹. ^e Ref. 9. ^f Ref. 10. ^g Refs. 11 and 12. ^h Ref. 13. ⁱ Refs. 11 and 14. ^j Ref. 15. ^k Ref. 16. ^l Ref. 17. ^m Experimental values taken from Ref. 7. ⁿ Experimental value taken from Ref. 8.

TABLE 3: Characteristics of Trimers^a

Species ^b	RO...O(Å)	θ	δ	E_{tot}/n^c
Double donor	2.99		0	-3.39
Double acceptor	2.99	0	0	-3.40
Sequential	2.98	0	0	-3.83
Cyclic	3.04	24±1	0	-4.32

^a $R_{O...O}$ is the average distance between the nearest neighbored oxygen atoms, angle θ is the deviation of hydrogen-bonded hydrogen from linearity, and angle δ denotes the inclination of hydrogen-bonded hydrogen from O-O-O plane. ^b Notations are the same as those in Figure 3. ^c Total interaction energy per molecule, units in kcal/mole.

TABLE 4: Characteristics of Tetramers^a

Species ^b	$R_{O...O}$	θ	δ	E_{tot}/n
Cyclic	3.03	24±1	5±2	-5.11
I	2.98	0	0	-4.16
II	2.98	0	0	-4.40
III	3.06	0	0	-4.04
IV	3.05	0	0	-4.80

^a Refer to footnotes in Table 3. ^b Notations are the same as those in Figure 4.

TABLE 5: Characteristics of Pentamers^a

Species ^b	$R_{O...O}$	θ	δ	E_{tot}/n
Cyclic	2.99	24±1	2±1	-5.94
I	2.98	0	0	-4.01
II	2.98	0	0	-4.29

^a Refer to footnotes in Table 3. ^b Notations are the same as those in Figure 5.

TABLE 6: Characteristics of Hexamers and Heptamers^a

	Species ^b	$R_{O...O}$	θ	δ	E_{tot}/n
Hexamer	Cyclic	2.96	24±1	0	-5.78
	I	2.98	0	0	-4.45
	II	2.98	0	0	-4.58
Heptamer	Cyclic	3.32			-2.56
	I	2.98	0	0	-4.65
	II	2.98	0	0	-4.68

^a Refer to footnotes in Table 3. ^b Notations are the same as those in Figures 6 and 7.

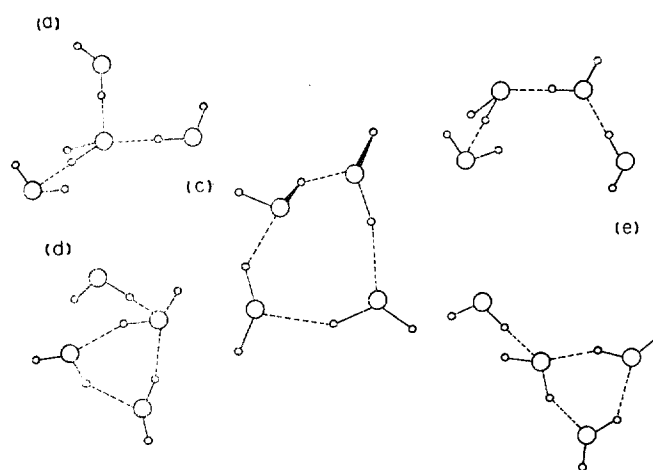


Figure 4. The structures of tetramer; (a) tetramer I, (b) tetramer II, (c) cyclic, (d) tetramer III, and (e) tetramer IV.

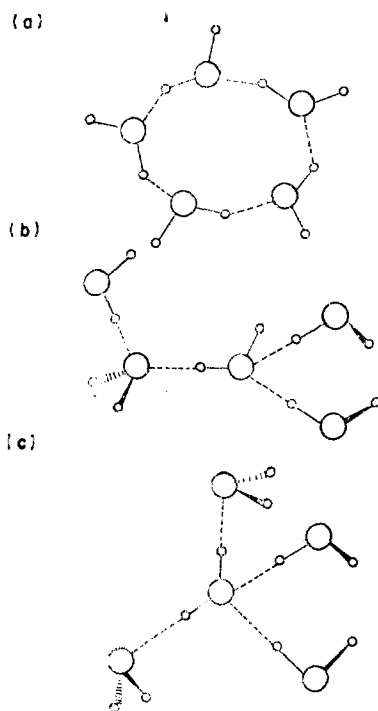
structure is probably more stable than open structures. Kistenmacher *et al.*¹⁹ reached the same conclusion with the more accurate minimization procedure by using AFHF potentials. The results of Scheraga *et al.*⁹ show that the pyramidal tetramer with six hydrogen bonds is the most stable structure and cyclic tetramer is more stable than open species. The pyramidal tetramer was found to be the most stable species in spite of having the highly strained hydrogen bonds. Although they thought that the stability of each hydrogen bond is sacrificed to maximize the number of hydrogen bonds, it may be not right since hydrogen bond can not be formed with the highly bent angle of hydrogen bond.^{1, 21-25} EPEN pyramidal tetramer having two broken hydrogen bonds would be similar to a puckered cyclic species of our REPFCA tetramer. The total interaction energy of REPFCA cyclic tetramer is -20.44 kcal/mole, which is similar to those of EPEN and AFHF, -21.12 and -20.54 kcal/mole, respectively. The typical structures of tetramers are shown in Figure 4 and the calculated results are given in Table 4.

4. Pentamer. The studies for pentamer have been carried out without considering its importance in water clusters. Scheraga⁹ and Clementi¹⁹ found that a simple cyclic pentamer shows no minimum in the interreaction energy map. But we found

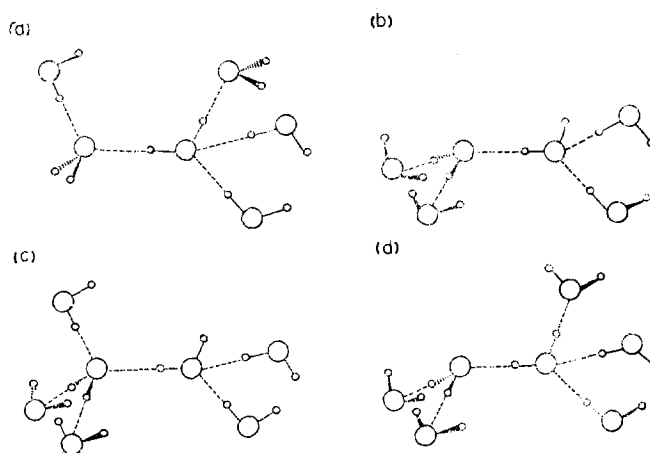
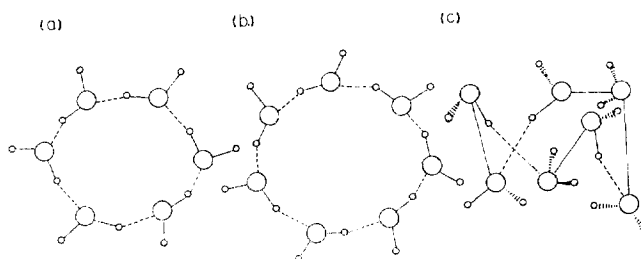
TABLE 7: The Relative Probabilities of Water Cluster per Molecule^a

	Species	E	$I^{1/2}$	p/p_0^b
Trimer	Cyclic	-4.32	76.16	0.081
	Double donor	-3.39	100.72	0.019
	Double acceptor	-3.40	100.49	0.019
	Sequential	-3.83	97.76	0.039
Tetramer	Cyclic	-5.11	206.51	0.273
	I	-4.16	305.03	0.061
	II	-4.40	344.98	0.094
	III	-4.04	136.98	0.041
	IV	-4.80	183.92	0.157
Pentamer	Cyclic	-5.94	485.25	1.000
	I	-4.01	622.60	0.041
	II	-4.29	590.34	0.065
Hexamer	Cyclic	-5.78	1017.99	0.703
	I	-4.45	1034.60	0.076
	II	-4.58	1173.18	0.096
Heptamer	Cyclic	-2.56	2259.08	0.003
	I	-4.65	1768.19	0.097
	II	-4.68	1854.94	0.103

^a Probabilities of various clusters are calculated at $T=300\text{ K}$; E is total interaction energy per molecule in units of kcal/mole and $I^{1/2}$ is the square root of principal moment of inertia in units of $\text{kg}^{3/2}$. $m^3 \times 10^{-69}$. ^b p_0 is the reference probability of cyclic pentamer.

**Figure 5.** The structures of pentamer; (a) cyclic, (b) pentamer I, and (c) pentamer II.

that a cyclic pentamer has a minimum and is the most stable one of the single cyclic species, and that cyclic pentamer may be a favorable unit in water cluster if exist. The second peak in the radial distribution function^{26,27} of liquid water shows the existence of a six-membered ring at lower temperature. As the temperature rises, five-membered rings exceed six-membered rings and then the second peak becomes simple. The result for cyclic pentamer conforms

**Figure 6.** The open structures of hexamer and heptamer; (a) hexamer I, (b) hexamer II, (c) heptamer I, and (d) heptamer II.**Figure 7.** The structures of cyclic hexamer and heptamer; (a) planar cyclic hexamer, (b) cyclic heptamer seen from the top, looking down at the ring, and (c) cyclic heptamer seen from the side.

this experimental evidence.

The typical structures of pentamers are shown in Figure 5. Cyclic pentamer is flat and the bent angles of hydrogen bond are nearly the same value (approximately 23°). Open pentamers have the structures that the geometry between two water molecules is "head to tail"¹⁶. The overall structures of pentamer I and II are similar to that of linear water dimer at equilibrium and to tetrahedral structure, respectively. The results for pentamers are shown in Table 5.

5. Hexamer and Heptamer. Kistenmacher *et al.*¹⁹ have studied for the configuration of the lowest energies of cyclic hexamer and heptamer. The two geometries obtained by them are nearly planar. Our results show that cyclic hexamer is nearly planar, whereas cyclic heptamer is highly puckered. The geometries and energies for cyclic hexamer and heptamer are shown in Table 6. The energy per molecule of cyclic hexamer is lower by 0.17 kcal/mole than that of cyclic pentamer. Cyclic heptamer shown in Figure 7 has only three hydrogen bonds and its interaction energy per molecule is much lower than that of cyclic pentamer or hexamer. From this results, it is found that water cluster composed of seven molecules or more may not normally form a single ring.

Also the calculations are performed for other structures of hexamer and heptamer. The structures and the energies of them are shown in Figure 6 and in Table 6, respectively. Since structures of heptamer I and II are nearly the same each other, their energies are also similar. Various open structures of hexamer and heptamer having a five-membered

ring have not been considered extensively. Since many structures with slightly different geometries have nearly the same energy values, the calculations are performed only for the representative structures of hexamer and heptamer.

6. *Relative Probability Distribution of Water Cluster.* Using the results of energy calculation of water clusters, the population of each cluster can be obtained. In general, the population of the i th cluster P_i can be expressed as

$$P_i \propto f_i^{\text{tr}} \cdot f_i^{\text{rot}} \cdot f_i^{\text{vib}} \cdot e^{-n_i E_i / RT} \quad (11)$$

where f 's are the partition functions for translational, rotational, and vibrational motions, E_i is the interaction energy for the i th cluster per molecule, and n_i is the number of molecules in the i th cluster.

Then, the ratio of P_i to P_j is given by

$$P_i / P_j = (f_i^{\text{tr}} \cdot f_i^{\text{rot}} \cdot f_i^{\text{vib}} / f_j^{\text{tr}} \cdot f_j^{\text{rot}} \cdot f_j^{\text{vib}}) e^{-(n_i E_i - n_j E_j) / RT} \quad (12)$$

It is assumed that the contribution of translational partition function to P_i / P_j is $m^{3(n_i - n_j) / 2}$ and the ratio $f_i^{\text{vib}} / f_j^{\text{vib}}$ is approximately $(RT)^{3(n_i - n_j)}$. Hence, the ratio P_i / P_j can be expressed in terms of mass of molecule, moment of inertia, symmetry numbers, and energies.

If the ratio of symmetry numbers is taken to be unity,

$$P_i / P_j = m^{3(n_i - n_j) / 2} \cdot I_i^{1/2} \cdot I_j^{-1/2} \cdot (RT)^{3(n_i - n_j)} \cdot e^{-(n_i E_i - n_j E_j) / RT} \quad (13)$$

Then, the relative probability of cluster per molecule can be expressed as

$$p_i / p_j = I_i^{1/2 n_i} \cdot I_j^{-1/2 n_j} \cdot e^{-(E_i - E_j) / RT} \quad (14)$$

The state of cyclic pentamer is taken to be the reference one and the relative probability of each cluster per molecule is shown in Table 7. From the analysis of relative probabilities of water clusters per molecule, cyclic pentamer is found to be the most probable species of water clusters. The relative probability of cluster per molecule increases until cluster size n becomes to five, and decreases when n is larger than five. Cyclic structures are more favorable than open structures, but cyclic heptamer is less stable than branched species due to the ring strain.

Interaction energies of cyclic and open water clusters as a function of cluster size n are shown in Figure 8. The minimum of interaction energy per molecule appears in the case of cyclic pentamer. These results are different from those obtained by Kistenmacher *et al.*¹⁹ that the greater a ring size is, the larger the value of energy per molecule is. But our results are in partial agreement with those of Del Bene and Pople¹⁶ that cyclic polymers are dominant structures. It is found that the large cyclic structures are more stable than their chain analogues since in cyclic structure the additional stability due to the additional hydrogen bond may surpass the instability resulted from the ring system. Del Bene and Pople¹⁶ have studied unbranched chain molecules composed of two to five molecules in geometrical pattern of "head-to-tail" and have found that the lengthening of chain continues to enhance the strength of hydrogen bond. But the pentamer obtained in such a configuration is a cyclic

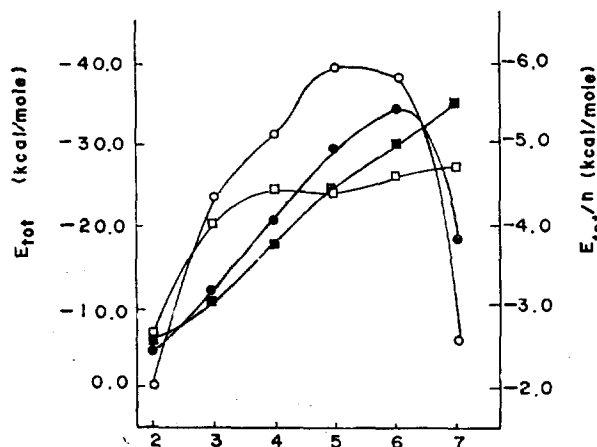


Figure 8. Interaction energies of $(\text{H}_2\text{O})_n$ clusters as a function of the cluster size n : \circ , energy per molecule of cyclic species; \square , energy per molecule of open species; \bullet , total interaction energy of cyclic species; \blacksquare , total interaction energy of open species.

pentamer having an additional hydrogen bond between the "head" and "tail" of chain pentamer. And an open hexamer could not be obtained from such a configuration. This fact is in good agreement with our results that an infinitely long chain of cluster may not exist.

Conclusion

The stability of water cluster containing two to seven water molecules is investigated by using a revised empirical potential function and the relative probability of water cluster per molecule is also discussed.

Generally, the more hydrogen bonds a cluster has, the higher stability it has as long as the hydrogen bond is not too much distorted. Adding one water molecule to any clusters brings the additional stability for chain cluster, but an infinitely long chain cluster may not exist. Cyclic structures are more stable than open ones except heptamer. Cyclic pentamer is found to be the most stable unit in water cluster.

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Bromine-Exchange Reaction of Antimony Tribromide with Benzyl Bromide in Nitrobenzene and in 1,2,4-Trichlorobenzene*

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The rate of the bromine-exchange reaction of antimony tribromide with benzyl bromide in nitrobenzene or 1,2,4-trichlorobenzene has been measured, using Br-82 labelled antimony tribromide. The result of the study indicates that the exchange reaction is first order with respect to benzyl bromide, and either second or first order with respect to antimony tribromide depending on its concentrations. The second-order kinetics with respect to antimony tribromide have been observed at relatively high [SbBr₃] concentrations, and the first-order kinetics at lower [SbBr₃] concentrations. Reaction mechanisms are proposed for the exchange reaction.

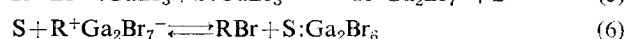
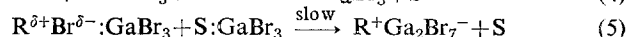
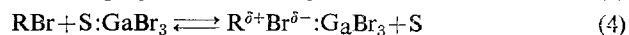
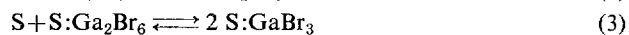
Introduction

In the previous papers of this series, we reported the results of the kinetic studies on the bromine-exchange reactions between gallium bromide and organic bromides in solution.¹⁻⁶ The organic bromides used for the kinetic studies were methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl and *i*-butyl bromides. Nitrobenzene and 1,2,4-trichlorobenzene were used as solvents.

The results of these studies indicated that all the exchange reactions were second order with respect to gallium bromide and first order with respect to the alkyl bromides examined.

$$\text{Rate} = k_3 [\text{GaBr}_3]^2 [\text{RBr}] \quad (1)$$

Reaction mechanism for the exchange reactions was also proposed in the previous papers.



The breaking of the carbon-bromine bond in the polarized molecules of the addition compounds of gallium bromide with alkyl bromides was assumed to be the slowest step among various reaction steps. Thus, step (5) was considered to be the rate-determining step of the exchange reactions. This mechanism would lead to the following kinetic expression:

$$\text{Rate} = k [\text{S}:\text{GaBr}_3]^2 [\text{RBr}]$$

*Abstracted, in part, from Ph.D. thesis of Young Il Pae, Sogang University, 1979, and from M.S. thesis of Sok Hwan Rhyu, Sogang University, 1981.

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