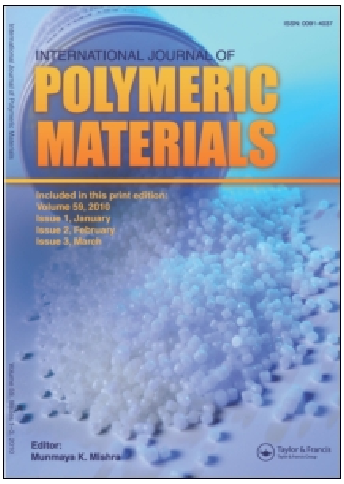

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Calculation of Some Structural Features of Polyethylene Oxide

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Calculation of Some Structural Features of Polyethylene Oxide

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Calculation are performed on seven units of ethylene oxide of molecular weight (44.05–309.37), using empirical and semi-empirical methods. Electronic indices such as, polarizability, total energy, charge-transfer energy are calculated using CNDO/2 method. The interaction energy contribution of these polymers with surrounded water molecules are calculated. The van der Waals radius, surface area, cavity surface area and molecular volume are calculated. A significant correlations are obtained between the calculated size indices and molecular weight of the polyethylene oxide. These regressions can be used to predict the size indices for polyethylene oxide of higher molecular weights.

INTRODUCTION

Knowledge about the structure of polymers is essential for a proper understanding of their chemical and physical behaviour and for studies of the mechanisms of polymer, forming or polymer-modifying reaction. Considerable progress has been made in recent years in the basic understanding of structure property relationships in the field of polymeric material.

Apolymeric substance is one made up of chains of repeating molecules, the units of a chain of monomers are usually identical. The chains are not totally rigid but may be flexible in various ways. All the physical technique used to describe the features of polymers at the molecular level, are affected by the nature of the polymer, since the manner in which organic group are connected in the segments to form a polymer appears to influence the shape and properties of the polymer.

Flory and Huggins[1,2] have shown that, all segments have the same volume but that different segments make different number of contacts because of their different surface. Hence, it is necessary to consider that equal volume will have different surface area due to their different shape.

In the liquid state, polymer molecules take up their most probable conformation through rotation about single bonds. The most stable conformation can be considered when the chains are fixed in their lowest energy conformation. This may be planar, zig-zag or helical depending upon external conditions, such as, temperature, elongation. The chains can be extended or folded.[3]

In the present work, the most reliable conformation of polyethylene oxide in solution is constructed. The van der Waals radius, surface area and volume for each segment in polyethylene oxide are calculated. In addition, some electronic indices relevant to the conformation stability and behaviour are also calculated using semi-empirical Molecular Orbital (MO) method.

SCOPE OF THE PRESENT STUDY

A computer program is developed to calculate van der Waals radius, surface area, volume and some electronic indices using empirical and semi-empirical methods. The great utility of such calculated indices is to predict physico-chemical properties of the polymer that can be used in the study of solution behaviour, by formulation a mathematical relationships between the calculated and observed properties of the polymer, such as solubility, heat of hydration.

In studies of hydrocarbon solubility in water, Hermann[4] developed a method for calculating the surface area inside the idealized solvent cavity required to accommodate the hydrocarbons solute. The calculated cavity surface area contains the centres of water molecules in the first layer around the solute, since, this cavity area has the properties of an envelope of enclosure, and depends upon the connectivity of the molecular skeleton.

The calculation of solvent interaction energies can be used in determining the stability in the environment of water molecules. There are many ways to model and calculate the effect of solvent on solute. The super molecule approach,[5] it concentrates on water molecules which are likely to be tightly bound by hydrogen bonds to the solute. The most stable position for water molecules in the environment of solute are found, their effect on the solute molecule conformation and overall interaction energy being deduced.

In the present study, the form of the polymer is taken into account, which is deduced from van der Waals radii of the atoms. The solvent molecules are represented by spheres of an approximate radius of 1.5 Å (for H_2O) which are packed around the polymer profile.

The van der Waals radii used to calculate the size indices are:

atom	radii (Å)
H	1.2
C	1.7
O	1.52

A solvent accessible shell is computed by adding the solvent radius to the van der Waals radius of each atom. The cavity surface area is calculated from the solvent accessible surface area.

The purpose of this study is to test properties relating to electronic properties of polyethylene oxide, such as, polarizability, total binding energy, and charge transfer energy. In addition, to calculate size and solute-solvent interaction energies. A simple regression analysis of van der Waals radius, surface area, and molecular volume with molecular weights is performed for the seven segments of polyethylene oxide.

EXPERIMENTAL

Calculations are performed on seven segments of ethylene oxide of molecular weight (44.05–309.3 gm/mol). The geometry and coordinates in space of all atoms of ethylene oxide and its repeating segments is determined by using standard bond lengths and bond angles,[6] and data obtained from an X-ray diffraction method reported in Ref. 7.

Three-dimensional atomic coordinates is used for electronic indices calculations, by transferring them into a quantum mechanical program (QCPE 261), to obtain the molecular orbital charge densities for the polymer. These results are used for the calculation of other electronic properties of the polymer.

The numerical computations were carried out on an IBM 4341 computer.

METHOD

The following Molecular Orbital (MO) properties are calculated using Complete Neglect Differential Overlap (CNDO/2) method. Frontier orbital energies (EHOMO, ELEMO). These are simply the eigenvalues associated with the highest occupied and lowest empty molecular orbitals respectively. EHOMO measures the electron donating ability, ELEMO measures the electron accepting ability, these energy levels are very important in determining the ease of formation of charge transfer complexes two species.

The total interaction energy of primary sheath of water molecules is calculated. The major contributions to the interaction energies are polarization, dispersion and cavity interaction terms. The fundamental property governing the former is polarizabilities (E_{pol1}, E_{pol2}) in a polymer. E_{pol1} is the interaction energy due to polarization of the solvent molecule (H_2O) by permanent dipole of the solute molecule (polymer). E_{pol2} is the interaction energy due to polarization of the solute molecule (polymer) by the permanent dipoles of solvent molecule (H_2O). The atomic polarizability relates to the volume of the atom, hence, the total molecular polarizability should bear a relationship to some topological property of the polymer molecule.

Molecular polarizability (pol) calculated by a simple summation of the atomic polarizability values obtained from Ref. 10 and are given in Table I, for each atom in the polyethylene oxide. By this means, polymer polarizability is determined for a single ethylene oxide and its repeating segments up 7 units, as shown in Table III.

TABLE I
Values of atomic polarizability

Atom	Polarizability ($Å^3$)
H	0.210
C	1.476
O	0.696

The cavity interaction energy is the energy required to form a cavity in the solvent to accommodate the solute molecule of volume (Vol). This can be expressed as γA, where γ is the surface tension of the solvent and A is the area of the surface of the cavity. Using the microscopic surface tension of water (which is evaluated from an empirical expression.[8] The following expression is obtained for cavity interaction term (E_{cav}):

$$E_{\text{cav}} = 0.00145 * \text{SA} \tag{1}$$

where SA is the surface area of a solid representation of molecule suggested by Bondi.[9] The size indices which is calculated in this work are all based on the model of Bondi. The van der Waals radius (RAD), van der Waals surface area (SA) and van der Waals volume (Vol) are the three parameters determined for each species in this study. RAD and SA are determined by dividing the surface of each atomic sphere into segments of area not greater than 0.1 Å. It is then determined which of these segments lie on the polyethylene oxide profile, the area of these segments being included into the surface area summations. The distance of the segment from the centre of mass of the molecule is used in mean van der Waals radius calculation.

In the polymer volume calculation, a rectangular solid is defined such that all of its faces touch the polyethylene oxide profile. The solid is segmented into cubes of side 0.1 Å. It is then determined which of these cube lie within the polyethylene oxide profile and a simple counting procedure is used to obtain the polyethylene oxide volume.

RESULTS AND DISCUSSION

Calculations are performed on seven segments (n) of ethylene oxide (Figure 1) of molecular weight (44.05–309.37) using empirical and

$$(CH_2—CH_2—O)n$$

FIGURE 1 Structure of polyethylene oxide.

semi-empirical methods. The cartesians of the polymers studies are obtained, using both standard bond length, bond angle and dihedral angles and X-ray data. The relative stability of these conformations are checked by calculating the total (ETOT) and binding (EBIND) energies for each polymer (in hartree), using complete neglect Differential overlap (CNDO/2) method, and are given in Table II. The convergence criteria is 1.0E-06 in the calculated successive energies. The geometry obtained from X-ray data is more stable and is used in the present work.

Dipole moment, polarizability (pol) and charge transfer interaction terms, Ionization potential (EHOMO), electron affinity (ELEMO) are calculated and are given in Table III. Values of 7.04 (e.v.) and 2.04 (Debye) are obtained for ionization potential and dipole moment respectively for ethylene oxide (cyclo form). The positive sign for the former indicates, the susceptibility of ethylene oxide for polymerization, polarizability is a quantity observed when a uniform electric field is applied to a polymer, the field gradiant from this has $1/r^3$ dependent, such that the field experienced by polymer becomes progressively more uniform, the greater the distance of water molecule from the polymer. This may be used to characterize the second order interaction at intermediate—polymer reagent separation. The number of water

TABLE II

Calculated total and binding energies for polyethylene oxide (all values are in Hartrea)

	−ETOT		−EBIND	
No.	X-ray	Standard	X-ray	Standard
1	35.82	35.68	2.22	2.72
2	71.63	71.60	5.06	5.02
3	107.18	107.34	7.64	7.81
4	142.90	143.11	10.40	10.61
5	178.64	178.85	13.17	13.38
6	214.31	214.50	15.87	16.16
7	248.71	250.28	17.30	18.87

TABLE III

Calculated electronic indices for polyethylene oxide

No.	EHOMO (e.v.)	ELEMO (e.v.)	Dipole m (D)	Pol ($Å^3$)
1	−22.70	−9.916	17.14	4.687
2	−18.63	−9.540	24.01	9.165
3	−17.20	−9.229	39.06	13.64
4	−16.43	−9.44	44.96	18.12
5	−15.83	−9.355	56.37	22.59
6	−15.42	−9.499	73.40	27.07
7	14.44	−8.723	84.39	31.55

molecules (H_2O no.) surrounded in the first and second sheaths of each polymer is calculated and are given in Table IV.

For contributions to the interaction energy of the polymer with water molecules are calculated. These are cavity (E_{cav}), polarizabilities (E_{pol1}, E_{pol2}), and London dispersion (E_{dis}) energies, and are given in Table IV.

Values of 1.48 (Debye) and 1.84 ($Å^3$) are used for dipole moment and polarizability of water molecule respectively.

It is noticeable that the contributions of E_{pol1} and E_{dis} have major contributions of the total interaction energy. The latter has an opposite trend, as the size of the polymer increases, its value decreases. The total interaction energy value increases with increasing the size of the polymer.

For the size indices, van de Waals radius (RAD), surface area (SA), volume (Vol) and cavity surface area (CSA) are calculated and are given in Table V.

TABLE IV

Calculated interaction energy contributions for polyethylene oxide (all values are in kcal/mole)

No.	E_{cav}	$-E_{pol_1}$	E_{pol_2}	$-E_{dis}$	$-E_{tot}$	H_2O no
1	0.1713	40.69	1.3360	30.07	69.26	29.24
2	0.3148	39.75	2.4618	33.26	70.24	41.83
3	0.4701	42.52	3.6152	32.73	71.17	53.77
4	0.6459	44.87	5.0084	30.65	69.87	66.42
5	0.8428	48.58	6.5894	25.43	66.58	78.75
6	1.0688	53.01	8.4103	20.04	63.57	91.56
7	1.5171	56.46	12.492	11.29	53.74	121.90

TABLE V

Calculated size indices for polyethylene oxide

No.	Mol wt gm/mol	Radius (Å)	SA ($Å^2$)	Vol ($Å^3$)	CSA ($Å^2$)
1	44.05	2.39	79.65	51.82	206.71
2	89.11	3.03	134.82	93.99	295.71
3	133.1	3.58	188.39	135.0	380.10
4	177.2	4.12	243.49	177.1	469.51
5	221.2	4.93	297.38	219.1	556.72
6	265.3	5.42	351.78	261.3	647.23
7	309.3	6.82	439.73	317.8	861.67

A simple regression analysis between these indices and molecular weight (m wt) of the polymers are performed. A significant correlations is obtained. Significance levels are above 99.9%. Standard errors of the slopes and the intercepts are given in parentheses.

$$\mathrm{RAD} = 0.0155(\pm 0.001)\ \mathrm{m\ wt} + 1.55(\pm 0.2)$$
$$\text{and} \quad r = 0.9846, \quad s = 0.28, \quad F(1, 5) = 158.2 \quad (1)$$

$$\mathrm{SA} = 1.31(\pm 0.04)\ \mathrm{m\ wt} + 16.03(\pm 9.4)$$
$$\text{and} \quad r = 0.9967, \quad s = 11.1, \quad F(1, 5) = 752.2 \quad (2)$$

$$\mathrm{CSA} = 2.296(\pm 0.1)\ \mathrm{m\ wt} + 81.98(\pm 358)$$
$$\text{and} \quad r = 0.9848, \quad s = 42.3, \quad F(1, 5) = 160.8. \quad (3)$$

$$\mathrm{Vol} = 0.982(\pm 0.02)\ \mathrm{m\ wt} + 5.67(\pm 4.2)$$
$$\text{and} \quad r = 0.9988, \quad s = 5.08, \quad F(1, 5) = 2043.7 \quad (4)$$

Here, r is correlation coefficient, s is the standard deviation, and F is the variance ratio.

These equations can be used to obtain van der Waals radius, surface area and volume of polyethylene oxide for higher molecular weights. This is because the computation of these indices are consuming in computing time.

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