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Conduction Mechanism for PAP and Comparison of Physical Properties of PAP with other Polyaniline–based Conducting Polymers

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Polyaniline perchlorate (PAP) was synthesized by the chemical oxidation of aniline using ferric perchlorate as a strong oxidant. The electrical conductivity of PAP was measured at temperatures from −170 to 25 °C. It is suggested from the conductivity measurements that the conduction mechanism for PAP is a polaron hopping conduction. From the dependence of resistivity on the reciprocal temperature, the activation energy was computed to be 0.072 eV. From the comparison of the ESR parameters and conductivity at 25 °C for the polyaniline–based conducting polymers, the conductivities of PAP, PATFB and PATS increase with increasing ΔH_{pp}, decreasing A/B ratio and decreasing g–value, respectively. It is shown by TGA results for PAP, PATFB and PATS that the maximum weight loss rates (Pr) are 0.185 (at 269 °C), 0.366 (at 324 °C) and 0.23 mg/min (at 338 °C), respectively.

Introduction

As shown by previous studies[1-5], many conjugated polymers have been produced in efforts to obtain conducting polymers with higher conductivity. In particular, conducting polymers doped with a variety of chemical species have been synthesized extensively to obtain systems having semiconducting or metallic properties. These materials are obtained by the electrochemical or chemical doping technique using electron acceptors or donors. Conducting polymers are important from a basic scientific point of view and for various technological applications. They are useful materials for batteries, microelectronic devices and electrochromic displays. They are also being applied in the new fascinating areas of condensed matter physics. Hitherto, many studies on anino- or cation- doped polymers produced by chemical or electrochemical doping methods have been reported. Examples of such polymers include polyacetylene, poly–p–phenylene and polypyrrole–based conducting polymers. Satisfying re-

sults have been obtained from these materials.

Chiang *et al.*[2] have reported that the electrical conductivity of halogen–doped polyacetylene can be increased by more than eight orders of magnitude. The associated thermal activation energy decreases from initial values of about 0.3 eV to 0.01 eV, and the maximum room temperature conductivity with iodine as dopant exceeds 500 (ohm–cm)⁻¹. Mermilliod *et al.*[3] reported that polypyrrole could be obtained by a very simple one–step chemical oxidation of monomer using a strong oxidant in various solvents. Studies on conducting polymers doped with the perchlorate anion can also be found in reports by Pfluger[1] and Mermilliod[3]. These researchers synthesized the polypyrrole perchlorate by chemical oxidation of pyrrole using a strong oxidant, ferric perchlorates. The oxidized polypyrrole is stable and can even be handled in air without changes in its electrochemical properties. Also, study of this chemically synthesized polypyrrole perchlorate has shown satisfying results in such applications as electrode materials for secondary batteries. Shirakawa *et al.*[6] reported

that the room temperature conductivity for crystalline films of polyacetylene depended on the *cis – trans*, content, varying from 10^{-5} (ohm-cm)$^{-1}$ for the *trans* – isomer to 10^{-9} (ohm-cm)$^{-1}$ for the *cis* one.

On the other hand, there are few reported studies on polyaniline–based conducting polymers. Thus, we have started studies on various anion–doped polyaniline, and reported results on the polyaniline tetrafluoroborate (PATFB)[7]. In this study, synthesis of polyaniline perchlorate (PAP) by the chemical oxidation of aniline using a strong oxidant, $Fe(ClO_4)_3$ was carried out and the conduction mechanism was determined.

In addition, the syntheses of polyaniline *p*–toluenesulfonate (PATS) and polyaniline tetrafluorobotate (PATFB) by the electrochemical oxidation of aniline were also undertaken for comparison of the physical properties of PAP with other polyaniline–based conducting polymers. We present here our results of the thermal stabilities, ESR measurements and electrical conduction mechanisms of these polymers.

Experimental

Materials. Ferric perchlorate, $Fe(ClO_4)_3 \cdot 9H_2O$ was obtained from Fluka Chemical Co. Tetraethylammonium *p*–toluenesulfonate and tetraethylammonium tetrafluoroborate used as supporting electrolytes were obtained from Aldrich Chemical Co. Before use, they were fully dried in a vacuum oven because of the hygroscopic natures of these materials. Aniline was purified by vacuum distillation.

Sample Preparation.

a) Polyaniline perchlorate (PAP): Aniline was polymerized in water using a strong oxidant, $Fe(ClO_4)_3$. Aqueous solutions of aniline (0.3 M) and $Fe(ClO_4)_3$, (0.7 M), were prepared. Each solution was cooled down to 0 °C. Oxygen dissolved in the solutions was removed by nitrogen bubbling for at least 30 min. When these solutions were mixed, a black precipitate of polyaniline immediately appeared. The mixture was kept at 0 °C under nitrogen bubbling and stirred for 2 hours. The precipitates obtained from this mixture were rinsed with distilled water and dried in a vacuum oven for 2 days at 40–50 °C. The polyaniline perchlorate (PAP) thus was obtained a black conducting powder which was stable in its oxidized state in air.

b) PATS and PATFB: Polyaniline *p*–toluenesulfonate (PATS) and polyaniline tetrafluoroborate (PATFB) were prepared from 0.2 M aniline in (1/99) (volume %) water/acetonitrile solutions containing 0.1 M tetraethylammonium *p*–toluenesulfonate (TEATS) and tetraethylammonium tetrafluoroborate (TEABF$_4$) as supporting electrolytes, respectively. These solutions were deoxygenated by nitrogen bubbling for 30 min before experiment. Using a Lauda Circulator, the temperatures of these systems were maintained at 25 °C.

The three–electrode electrochemical cell system was composed of a Pt working electrode, a Pt counter electrode and a standard calomel electrode. The working electrode was a 2 cm^2 Pt plate, and a 1 cm long Pt cylinder was used as the counter electrode. PATS and PATFB were electrochemically obtained at potentials of 1.5 V and 1.8 V, respectively. The anodic precipitates produced from this electrochemi-

Table 1. Elemental Analysis for Various Polyaniline-based Polymers

Polyaniline derivatives	Polymer chains (%)			Dopant (%)
	C	H	N	
PATS	37.90	2.99	7.80	51.29
PATFB	51.00	4.10	9.93	34.97
PAP	35.11	3.08	6.92	54.89

cal reaction remained on the electrode as insoluble materials, and they were confirmed to be the electrically conductive polymers. These products were removed from the anodic electrode, rinsed with acetonitrile, and dried in a vacuum oven for 2 days. Elemental analyses of PAP, PATFB and PATS were performed to determine the dopant contents in the polyaniline–based conducting polymers. The result is shown in Table 1.

Conductivity Measurements. Electrical conductivity was measured by a four–probe technique at temperatures from –170 to 25 °C. The current and voltage were measured by a Keithley 616 Digital Electrometer and a 642 Digital Multimeter, respectively. Before experiments, the specimen was heat–treated at a temperature near the melting point to remove residual trapped carriers or dipole orientation effects.

The sample was placed in a temperature–controlled chamber and the required low temperature was obtained by using a liquid nitrogen stream surrounding the sample basket. The conductivities were calculated directly from the measured resistance and sample dimensions.

ESR Measurements. Electron spin resonance (ESR) measurements were performed using a Bruker EPR spectrometer (Model No. ER 200 E-SRC). Powder samples were placed in the ESR tube and ESR measurements were performed at 25 °C under suitable conditions.

Thermal Analysis. Thermogravimetric analysis (TGA) was performed using a thermal analyzer (Rigaku, Model No. 8150). TGA measurements for PAP, PATFB and PATS were performed in the temperature range of 25–800 °C with a heating rate of 10 °C/min under a nitrogen atmosphere.

Results and Discussion

Conduction Mechanism. Generally, organic conducting polymers have overlapping sets of molecular orbitals which provide reasonable carrier mobility along the polymer chains. Since most organic polymers do not have intrinsic charge carriers, appropriate charge carriers must be provided by some extrinsic method called as doping. Since charge carriers in the conducting polymer proceeds along the polymer chains three–dimensionally, an understanding of mechanisms for interchain transport is important.

Previous investigators have obviously predicted that a number of factors such as the chain planarity, degree of crystallinity, chain kinks and crosslinks affect interchain transport. In addition, the electronic coupling between chains can be affected by the dopant ion, both its size and shape can control the structure of dopant–polymer arrays. This coupling may be further enhanced by appropriate orbital overlap between dopant molecules and polymer chains.
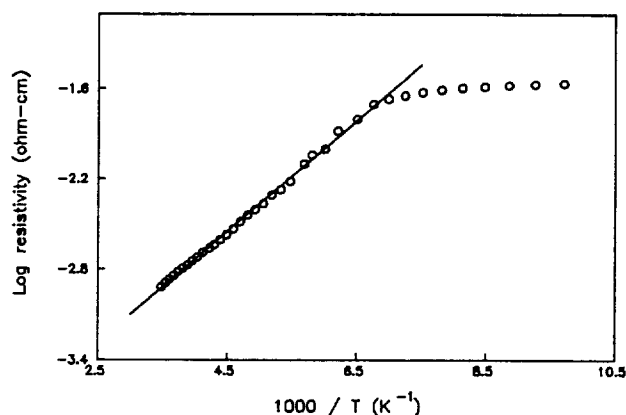
Figure 1. The temperature dependence of electrical resistivity for a polyaniline perchlorate.

Figure 2. The temperature dependence of electrical conductivity for a polyaniline perchlorate, according to the hopping conduction mechanism.

As mentioned above, no fully reasonable conduction mechanism has yet been suggested because of the various factors which influence conductivity such as the dopant level, morphology of the polymers, orientation of the conducting species, temperature, density, shape and the applied voltage. Also, the crystalline–amorphous phase boundaries in polymers show the largest deviations from ideal behavior, and band structure can not be used for an amorphous matrix.

In many reports[8-12] investigators have suggested equations relevant to specific composites. Possible models for electrical conduction in these composites have been reported with reasonable explanations and substantiating experimental results. Equations for the temperature dependence of electrical conductivity in disordered systems based on the hopping conduction mechanism have been given by Mott[8] and Greaves[9].

Mott's equation is based on a model in which charge is transported by the thermally assisted hopping of electrons between states localized near randomly distributed "traps"-potential fluctuations that can bind electrons. Also, it is reported that Mott's equation can be applied in the temperature range from −213 to 27 °C[10]. However, this equation is based on the assumption that the concentration of charge carriers has nothing to do with the temperature.

Greaves *et al.*[9] have suggested variable range hopping conduction represented by the following equation,

$$\sigma \cdot T^{1/2} = \exp(-(B/T^{1/4})).\qquad(1)$$

According to Mataré *et al.*[11], the temperature dependence of electrical conductivity which has been derived for a system including grain boundary barriers is given by the following eqn.,

$$\sigma = AT^{1/2} \cdot \exp(-Ea/kT).\qquad(2)$$

Also, tunneling[12] and thermionic emission conduction[13] can be expressed by the following two equations, respectively,

$$\sigma = \sigma_0 \cdot \exp(-A'/T^{1/2})\qquad(3)$$

and

$$\sigma = \sigma_0\, T^{-1/2} \cdot \exp(-Ea/kT).\qquad(4)$$

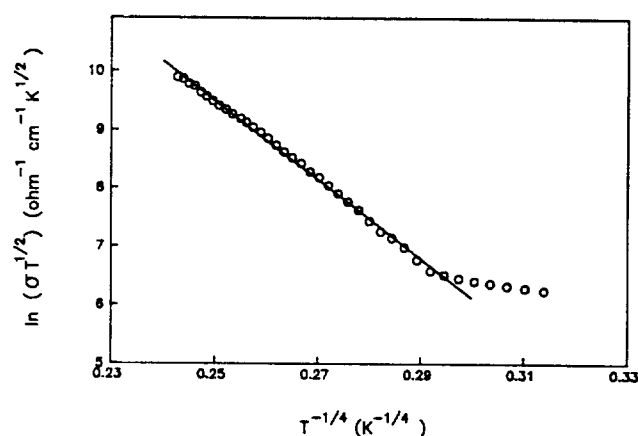**Conductivity Measurements.** PAP synthesized by the chemical oxidation of aniline was dried in a vacuum and

made into a pellet under a pressure of 0.8 tons/cm². The specimen was disc-shaped, 13 mm in diameter and 1.6 mm thick. The average density of the sample obtained using a pycnometer was 9.19 g/cm³. Measurements of the electrical conductivity of this PAP sample were performed by the four–probe technique at temperatures from −170 to 25 °C under low applied field to ensure ohmic behavior.

The temperature dependence of the measured resistivity for the pellet sample is shown in Figure 1. As shown in Figure 1, log resistivity decreases linearly with increasing temperature, satisfying the Arrhenius equation. $\rho = \rho_0 \cdot \exp(-E_a/kT)$ above −130°C. E_a was also calculated from the slope of the straight line in Figure 1 and was 0.072 eV. The value of log σ at 25 °C was evaluated to be 3.1 (ohm–cm)⁻¹.

This conductivity value obtained at 25 °C shows a remarkable increase over the reported value [log σ = 2 (ohm–cm)⁻¹] of pure polyaniline[14,15]. It is a satisfying increase of conductivity compared to the value [log σ = 2.4(ohm–cm)⁻¹] reported in our studies for PATEB[7]. The increase in conductivity suggests that the perchlorate anion creates a positive atmosphere which may be assumed to be a polaron state.

The various possible theoretical temperature dependencies of the electrical conductivity for PAP were determined using equations (1-4) for hopping, grain boundary, tunneling and thermionic emission conductions. Among these plots the hopping conduction mechanism shown in Figure 2 has the best linearity compared to those for the other conduction mechanisms. So, it can be suggested that the conduction in PAP is predominantly by hopping conduction. That is, the polarons formed in the polyaniline by doping with perchlorate anions, act as charge carriers and hop from chain to chain.

ESR Measurements. Recently, many ESR measurements[16-18] have been performed on conjugated polymers to investigate the magnetic properties of the electronic systems. The various parameters of ESR spectra for organic polymers depend on the physical and magnetic properties of these polymers. That is, analyses of the static and dynamic characteristics of paramagnetic species are possible from such spectrum parameters as multiplicity, position, shape, linewidth, intensity and symmetry. Also, it is reported that
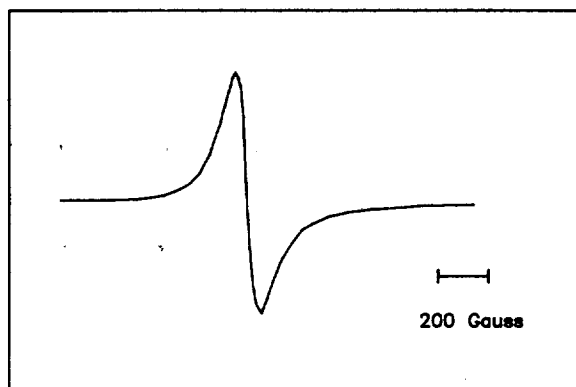
Figure 3. ESR spectrum of a polyaniline perchlorate at 25 °C (microwave frequency: 9.44 GHz).
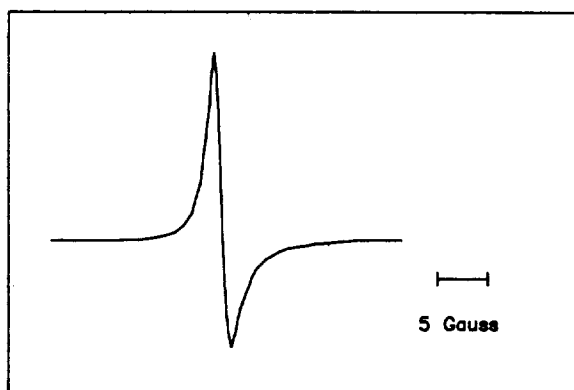
Figure 4. ESR spectrum of a polyaniline tetrafluoroborate at 25 °C (microwave frequency: 9.45 GHz).
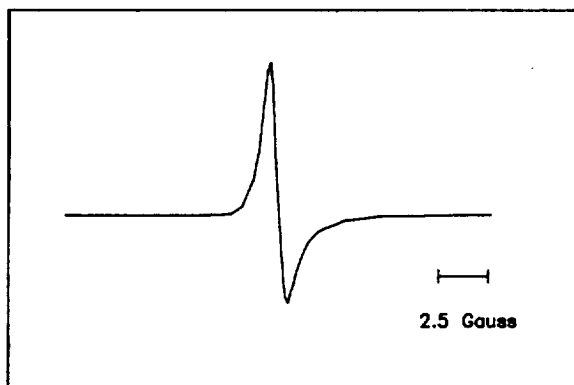

Figure 5. ESR spectrum of a polyaniline p-toluenesulfonate at 25 °C (microwave frequency: 9.45 GHz).

the peak-to-peak linewidth (ΔH_{pp}), A/B ratio and g-value in ESR spectra of conducting polymers may be related to the value of the conductivity[17].

Therefore, polyaniline tetrafluoroborate (PATFB) and polyaniline p - toluenesulfonate (PATS) were synthesized by the electrochemical doping process in order to compare the ESR parameters with conductivity for various polyaniline-based conducting polymers. ESR spectra of PAP, PATFB and PATS at room temperature are shown in Figures 3, 4 and 5, respectively and show single ESR peaks like those of most conducting polymers.

Table 2. Comparison of ESR Parameters and Log Conductivity at 25 °C for Various Polyaniline-based Polymers

Polyaniline derivatives	A/B ratio	ΔH_{pp} (Gauss)	g-value	Log conductivity (ohm-cm)[-1]
PAP	1.134	90.00	2.00104	3.154
PATFB	1.714	19.50	2.00465	2.428
PATS	1.753	0.75	2.00475	1.911
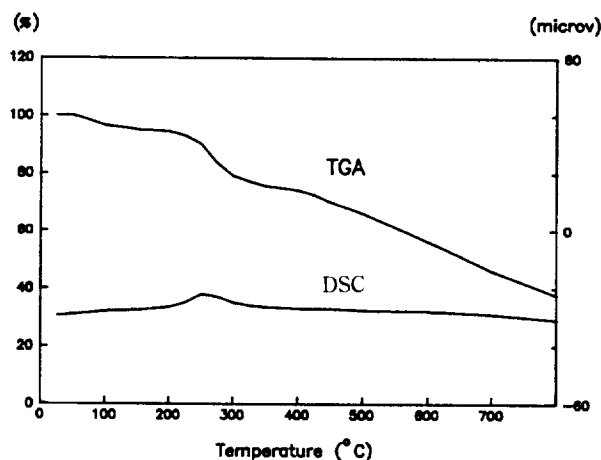
Figure 6. TGA and DSC curves of a polyaniline perchlorate in nitrogen.

Comparison of the ESR parameters and conductivity at 25 °C for these polymers is summarized in Table 2. It is evident from Table 2 that the conductivity of the polymers increases with increasing ΔH_{pp} and decreasing A/B ratio and decreasing g-value.

Thermal Analysis. Thermal analyses, (TGA and DSC) are needed to obtain information on the thermal and physical properties of conducting polymers. From the previous report[19], it has been known that the conductivities of conducting polymers increase with temperature prior to the final irreversible decomposition of the polymers. Also, it has been reported that the degree of change in conductivity and the decomposed temperature depend on the anion[4]. Thus, in this paper TGA measurements on the polyaniline-based polymers obtained by different doping methods (electrochemical or chemical technique) were performed to investigate their relative conductivity and thermal characteristics.

TGA and DSC curves for PAP, PATFB and PATS samples in the temperature range from 25 to 800 °C are shown in Figures 6, 7 and 8, respectively. As shown in the Figures, the temperature ranges (ΔTr) in which there were the most weight losses in PAP, PATFB and PATS were 277~352, 250~350 and 280~380 °C, respectively. Also, from the differential scanning calorimeter (DSC) results, an exothermic peak at 253 °C is found for the PAP sample.

Figure 9 is a plot of the weight loss (dW/dt) against the reciprocal of the absolute temperature for each sample. It is clearly shown in Figure 9 that the maximum weight loss rates(Pr) for PAP, PATFB and PATS are 0.185 (at 269 °C), 0.366 (at 324 °C) and 0.23 mg/min (at 338 °C), respectively. These TGA results for the samples are summarized in Table
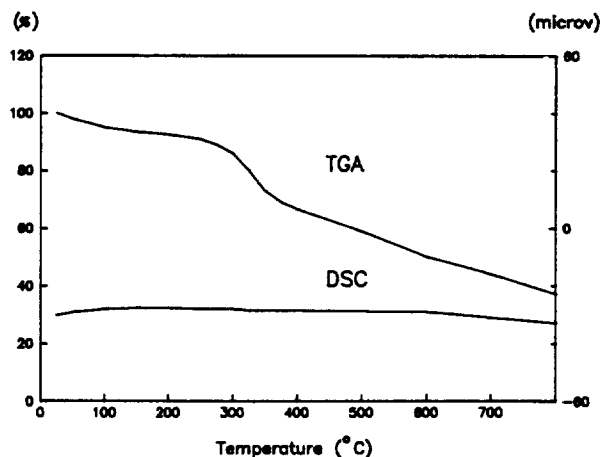
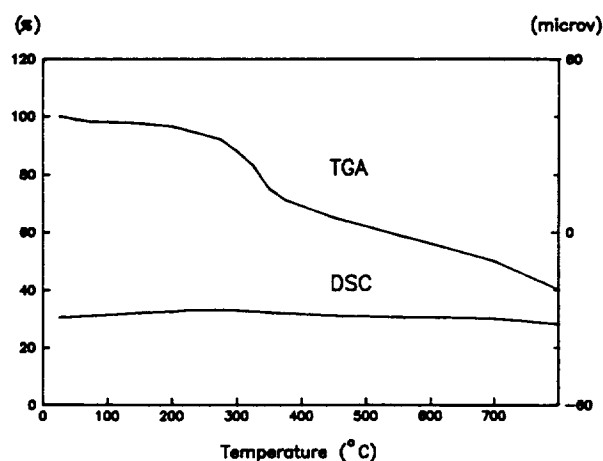**Figure 7.** TGA and DTA curves of polyaniline perchlorate in nitrogen.

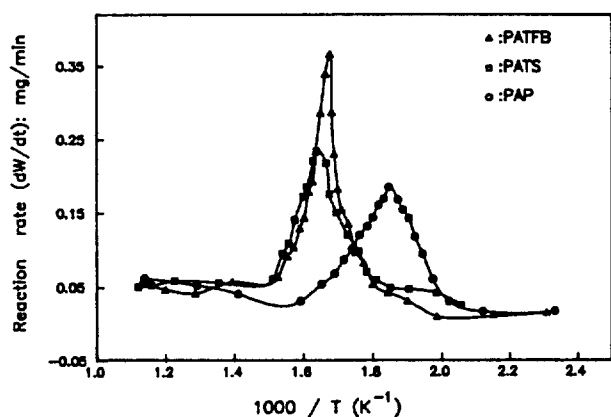**Figure 8.** TGA and DSC curves of a polyaniline p-toluenesulfonate in nitrogen.

Figure 9. The temperature dependencies of the reaction rate for various polyaniline based-polymers.

3 together the conductivities at 25 °C.

As shown in Figure 9 and Table 3, the thermal decomposition of the PAP polymer with higher conductivity begins at a lower temperature than for the polymers with lower con-

Table 3. TGA Results and Log Conductivities at 25 °C for Various Polyaniline-based Polymers

Polymer	Pr (mg/min)	Δ Tr (°C)	Log conductivity $(ohm-cm)^{-1}$
PAP	0.185 (at 269 °C)	227–352	3.154
PATFB	0.366 (at 324 °C)	250–350	2.428
PATS	0.230 (at 338 °C)	280–380	1.911

ductivity and progresses at a lower rate over a broader temperature range. Diaz and Hall[4] have also reported that the thermal decomposition of polymers with the higher conductivity begin at a lower temperature.

Figure 9 shows that the thermal decomposition of electrochemically oxidized conducting polymers begins at a higher temperature than that of chemically oxidized polymers. It also shows abrupt progression of the thermal decomposition compared to the case of chemically oxidized polymer.

Conclusions

Based on electrical conductivity measurements over the temperature range from –170 to 25 °C, the suggested conduction mechanism and charge carriers for PAP are the hopping conduction and polarons, respectively. Also, E_a for PAP obtained from the plot of electrical resistivity against temperature was 0.072 eV.

Comparison of the ESR parameters and conductivity at 25 °C for polyaniline–based conducting polymers (PAP, PATFB and PATS) shows that the conductivities of these various polymers increase with increasing ΔH_{pp} and decreasing A/B ratio and decreasing g-value.

From the thermal analyses for PAP, PATFB and PATS, the maximum weight loss rates (Pr) obtained were 0.185 (at 269 °C), 0.366 (at 324 °C) and 0.23 mg/min (at 338 °C), respectively.

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Structure and Activity of Quinolone Antibacterial Agents. 1. 7-Substituted 1-Ethyl-6-fluoro-1,4-dihydro-4-oxoquinoline-3-carboxylic Acids

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To find out a correlation between antibacterial activity and physical properties of 7-substituted 1-ethyl-6-fluoro-1,4-dihydro-4-oxoquinoline-3-carboxylic acid, dipole moments, charge distributions, and hydrophobicities were calculated. The atomic charges and the dipole moments to not give any correlations with inhibition of DNA gyrase, but the calculated hydration free energies show some correlations.

Introduction

The quinolone-carboxylic acids as antibacterial agents have been extensively explored for the broad spectrum antibacterial activity and orally effective drugs. Since nalidixic acid, the earlier type of the series of these compounds, was introduced in chemotherapy, there have been many efforts to develop the new powerful antibacterial agents.[1]

In recent years, the quantitative structure–activity relationships (QSAR) associated with the quinolones has been increasingly used in drug design. Typically, the predominant variables which are evaluated for correlation with biological activity are usually physicochemical parameters.[2] And the successful applications of the computer automated structure evaluation (CASE) which utilized molecular features inherent within the chemical structure were recently reported by Klopman *et al.*[3]

To explain a mechanism of inhibition of DNA gyrase by quinolone antibacterial agents, a cooperative quinolone–DNA binding model has been proposed.[4] The essential feature of the model is that bound gyrase induces a specific quinolone binding site in the relaxed DNA substrate in the presence of ATP. The proposed functional domains of quinolone antibacterial agents include hydrogen-bonding domain, drug–drug self-association domain, and drug–enzyme interaction domain.

In this work, we have calculated the physical properties such as dipole moment, charge distribution, and hydrophobicity of quinolone analogues. The calculated dipole moments and the charge distributions were used to find out the characteristics of the hydrogen-bonding domain in the molecules, and hydrophobicities were used to characterize drug–drug self-association domain. The aim of this work is to find out the correlations between biological activity and the calculated data, and to design new drugs.

Methods

The selected parent molecule 1-ethyl-6-fluoro-1,4-dihydro-4-oxoquinoline-3-carboxylic acid and its 7-substituted analogues were studied in this work. Their chemical structures are shown in Figure 1. The initial conformations of the selected quinolones were obtained by building, editing, and minimizing the molecules with Alchemy II.[5] Each conformation was refined with MMPMI,[6] which is an extension of MM2 and MMPI molecular mechanics programs. For each lowest-energy conformation, the atomic charges and the dipole moment were calculated with CNDO/2 (ON) method.[7] The hydration free energy of each group of the molecule was computed using the hydration shell model of Kang *et al.*[8] Especially, the hydration shell parameters of hydration shell radius (R_h) and the free energy density of hydration (Δg_h) for F atom were newly determined from best fitting the calculated free energies of hydration of CHF_3 and CF_4 to experi-