

TABLE 4: Hammett ρ_N and Brønsted β Values for the Reaction of Dansyl Chloride with Anilines at 30.0°C

	ρ_N	β
MeOH	-2.22	0.80
EtOH	-2.36	0.85
1-PrOH	-1.65	0.60
2-PrOH	-1.36	0.49
1-BuOH	-1.11	0.40
MeCN	-1.98	0.72

Correlation coefficients: $r > 0.998$.

considerably smaller than those for the reactions of 1- and 2-naphthalenesulfonyl chloride with anilines in acetone. ($\rho_N = -4.2$ and -4.6 , $\beta = 1.6$ and 1.8 respectively). Substitution of a dimethylamino group at the carbon 5 seems to reduce positive charge on the sulfur atom so that the degree of bond formation is decreased substantially compared with that for naphthalenesulfonyl chlorides. The size of both $|\rho_N|$ and β in various solvents decrease in the order EtOH > MeOH > MeCN > 1-PrOH > 2-PrOH > 1-BuOH. It is noteworthy that the $|\rho_N|$ and β values in MeCN are smaller than those in EtOH and MeOH while they are greater than those in other alcohols. Reference to Table 3 reveals that MeCN has the greatest values of ϵ and π^* but the smallest values of α among the solvent studied; polarity of solvent is not a sole factor in determining the TS, but HBD acidity (α) also contribute to the TS formation. This is clear from the relative importance of the two solvatochromic parameters, α and π^* , shown in Table 3.

According to the reactivity-selectivity principle (RSP)⁸, the greater the rate the less is the selectivity. Inspection of Tables 1 and 4 reveals that the RSP is not adhered in the present work, since a solvent of greater reactivity has also a greater selectivity (β and $|\rho_N|$).

We conclude that the reaction of dansyl chloride with anilines proceeds via an associative S_N2 mechanism, having somewhat similar TS structure with that of the benzenesulfonyl chloride reaction.

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Reference

- (1) Part 19 of the series "Nucleophilic Displacement at Sulfur Center". For part 18, see I. Lee and I. S. Koo, *Tetrahedron*, **39**, 1803 (1983).
- (2) (a) M. L. Tonnet and A. N. Hambly, *Aust. J. Chem.*, **24**, 703 (1971); (b) R. Foon and A. N. Hambly, *Ibid.*, **24**, 713 (1971); (c) I. Lee and I. S. Koo, *J. Korean Chem. Soc.*, **25**, 7 (1981); (d) I. Lee and I. S. Koo, *Bull. Korean Chem. Soc.*, **2**, 41 (1981); O. Rogne, *J. Chem. Soc. (P)*, 1294 (1968), *Ibid.*, 663 (1969), *Ibid.*, 1855 (1971), *Ibid.*, *Perkin* **2**, 472 (1972); (e) I. Lee and I. S. Koo, *Tetrahedron*, **39**, 1803 (1983).
- (3) (a) L. M. Litvinenko, A. F. Popov, and V. A. Savelova, *Ukr. Khim. Zr.*, **33**, 57 (1967); (b) L. M. Litvinenko, N. T. Maleeva, V. A. Savelova, and T. D. Kovach, *Zh. Obshch. Khim.*, **41**, 2615 (1971); (c) E. Ciuffarine, L. Senatore and, M. Isola, *J. Chem. Soc. Perkin* **2**, 468 (1972); (d) L. J. Stangeland, L. Senatore and E. Ciuffarin, *Ibid.*, 852 (1972); (e) A. Arcoria, E. Maccarone, G. Musumarra, and C. A. Tomaselli, *J. Org. Chem.*, **24**, 3595 (1974); (f) A. Arcoria, P. P. Ballistreri, G. Musumarra, and G. A. Tomaselli, *J. Chem. Soc. Perkin* **2**, 221 (1981).
- (4) F. B. Armstrong, "Biochemistry," 2nd Ed., p. 91. Oxford University Press, New York, 1983.
- (5) (a) K. Massie, *J. Org. Chem.*, **22**, 333 (1957); (b) H. F. Smith, *Amer. Ind. Hyg. Assoc. J.*, **23**, 95 (1962); (c) B. I. Ardashov, *J. Gen. Chem. (U.S.S.R)*, **21**, 1503 (1951); R. Weidenhagen and G. Train, *Ber.*, **75**, 1936 (1942).
- (6) (a) E. C. Evers and A. G. Knox, *J. Amer. Chem. Soc.*, **73**, 1739 (1951); (b) A. W. Stout and H. A. Schuette, *Ind. Eng. Chem. Anal., Ed.* **5**, 100 (1933); (c) R. J. Ozol and C. R. Materson, U. S. Pat. 2356689, Aug. 22, 1944 (Chem. Abs., **39**, 86 (1945)); (d) J. Clarke, R. Robinson, and J. C. Smith, *J. Chem. Soc.*, 2647 (1927); (e) J. Timmermans and Gillo, *Roez. Chem.*, **18**, 812 (1938).
- (7) I. Lee, I. S. Koo, B. D. Chang, and D. H. Kang, *Bull. Inst. Basic Sci. Inha Uni.* **6**, in press.
- (8) See for example, (a) A. Pross, *Adv. Phys. Org. Chem.*, **14**, 69 (1977); (b) C. D. Johnson, *Chem. Rev.*, **75**, 755 (1975); (c) D. J. McLennan, *Tetrahedron*, **34**, 2331 (1978); (d) C. D. Ritchie, *Acc. Chem. Res.*, **5**, 348 (1972).

Fluorescence of Styrene and Acrylic Acid Copolymers Containing Eu^{3+} in Tetrahydrofuran Solution

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The fluorescence emission of polystyrene-acrylic acid copolymers containing Eu^{3+} in tetrahydrofuran solution was investigated by spectrofluorimetry. The excimer emission increased linearly with the polymer concentration up to approximately $5 \times 10^{-2} \text{M}$. Benzene and toluene collisionally quenched the excimer fluorescence and their rate constants of quenching were determined. Quenching efficiencies decreased in the order: naphthalene > toluene > benzene. Analyses of Rayleigh scattering and europium emission showed no measurable structural changes observed under the experimental conditions.

Introduction

The fluorescence of the synthetic polymers with pendant aromatic groups is characterized by excimer emission. Excimer¹ results from the interaction of a group in an electronically excited state with a ground state of the same chromophore. Excimers have a lifetime in the range of 10–100nsec and their fluorescence is manifested in the appearance of broad structureless, Gaussian band at lower energy than that of an isolated aromatic ring. It has been demonstrated that excimer formation in dilute solutions is mainly caused by the intramolecular association between chromophores of nearest neighbor on the same polymer chain².

Recently the properties and structures of synthetic polymers containing metal ions have been extensively investigated³. An important class of metal ions are rare earths. Interest in lanthanides has been stimulated by their fluorescence and laser properties⁴. The results from studies on such as energy transfer and fluorescence intensity versus metal ion contents support a proposed model of ion-containing polymers consisting of clusters or aggregates of ionic groups dispersed throughout the system⁴.

Among a host of techniques including X-ray scattering, electron microscopy, and Raman spectroscopy, fluorescence measurements offer particular advantage since they are very sensitive. Fluorescent techniques have proved to be powerful methods for obtaining detailed information on the molecular structure of biopolymers and synthetic polymers^{5,6}. The aim of the present work is to extend previous investigations and to obtain a more intimate knowledge of the excimer in the presence of a small amount of aromatic solvents and to seek any analytical applications of spectrofluorimetry to synthetic polymers.

Experimental

Styrene-Acrylic Acid Copolymer (PSAA) A mixture of styrene (Kanto), acrylic acid (Fisher), and azobisisobutyronitrile (Wako) initiator at a mole ratio of 90:10:0.1 was weighed and placed in a polymerization tube. The copolymer was prepared as described in the literature^{3d}. The purification of the copolymer obtained was repeated four times. Elemental analysis showed that they yield was 60% and the mole % of styrene and acrylic acid were 87% and 13%, respectively.

PSAA-Eu Complex. Eu₂O₃ (Merck) was dissolved in concentrated HNO₃ and the solution was heated to 150°C⁷. Dissolution and evaporation cycle was repeated four times to ensure complete conversion to europium nitrate. A solution of weighed Eu(NO₃)₃ in ethanol and methyl ethyl ketone (1:1) was prepared and added to a PSAA solution in methyl ethyl ketone. The complex was synthesized and purified as described^{3d}. The complex was ashed in an electric furnace at 550°C and dissolved in HNO₃ to analyze europium contents by spectrofluorimetry using the standard addition method.

Instruments. A Hitachi model 650-60 spectrofluorimeter was used to measure fluorescence spectra of PSAA and PSAA-Eu. The measurements were carried out in tetrahydrofuran (THF) at room temperature. HPLC grade of benzene (Merck) and toluene (Matheson and Coleman), and naphthalene (Kanto)

were used as excimer quenchers. Absorption spectra were recorded on a Cary 17D spectrophotometer whose spectral response was calibrated with KMnO₄ solutions. The coordination structure of PSAA-Eu complex was identified by IR spectra using a Perkin-Elmer model IR 710B. DSC measurements were carried out using a Du Pont 910 analyzer.

Results and Discussion

The polymers, PSAA and PSAA-Eu, have an absorption maximum at 260nm in either dichloromethane or THF. The absorption spectrum of PSAA-Eu complex was almost identical to that of PSAA except Eu absorption near 394nm. The IR spectrum of PSAA has the characteristic carbonyl absorption at around 1700cm⁻¹. On formation of PSAA-Eu complex a new peak appeared at 1550cm⁻¹ corresponding to carboxylate ion absorption while carbonyl absorption decreased, which implied some protons on carboxylic acid groups in PSAA exchanged with Eu³⁺ ion. DSC measurements showed both PSAA and PSAA-Eu to have a glass transition temperature near 120°C and to be stable up to 300°C.

Figure 1 displays typical fluorescence emission spectra of PSAA-Eu complex excited at 260nm as a function of the complex concentration in THF. The bands at 260nm correspond to the Rayleigh scattering, whereas broad bands occurring at 328nm arise from excimer fluorescence. In addition, each spectrum consists of two shoulders at around 283 and 294 nm due to Raman scattering and monomer fluorescence, respectively. Raman scatter is emitted from THF. At high styrene contents in the polymer the intensity of monomer was considerably weaker than that of excimer. Because the monomer fluorescence intensity was difficult to extract from the spectrum of the complex, the ratio of excimer to monomer fluorescence intensity was not utilized to identify the mechanism of the excimer formation and to elucidate the local mobility of the polymer segments⁸. The increase in the PSAA-Eu concentration as styrene repeat-unit results in the enhancement both of excimer fluorescence and Rayleigh scattering, but no spectral shift observed.

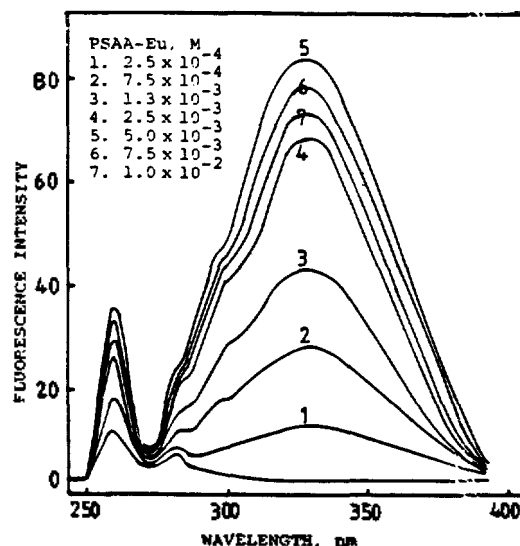


Figure 1. Fluorescence emission spectra of PSAA-Eu complex excited at 260nm in THF versus the complex concentration.

ed. The enhancement of excimer emission without spectral shift may be due to (a) the increase of viscosity of the solution, (b) the change of the refractive index, and (c) the increase of excimer formation. However, two of them are considered being negligible compared to the last one⁹. The relationship between excimer intensity and complex concentration is plotted in Figure 2. The excimer intensity increases linearly with increasing the polymer concentration up to approximately $5 \times 10^{-3}M$, within which analytical application seems to be possible. Deviation from linearity is typical of concentration quenching of fluorescence^{3c}. In order to exclude intermolecular effects, measurements were performed on dilute solutions of the PSAA-Eu complex hereafter.

Effects of Benzene and Toluene on Excimer. When a small amount of benzene or toluene was added to the solution of the PSAA-Eu complex in THF, the excimer intensity at 328nm was reduced. Figure 3 shows a typical variation in the fluorescence emission spectra depending on benzene concentration. The decrease in excimer intensity is remarkable. We notice that the monomer intensity at around 294nm seems to exhibit a very weak increase at lower benzene concentrations and buried under

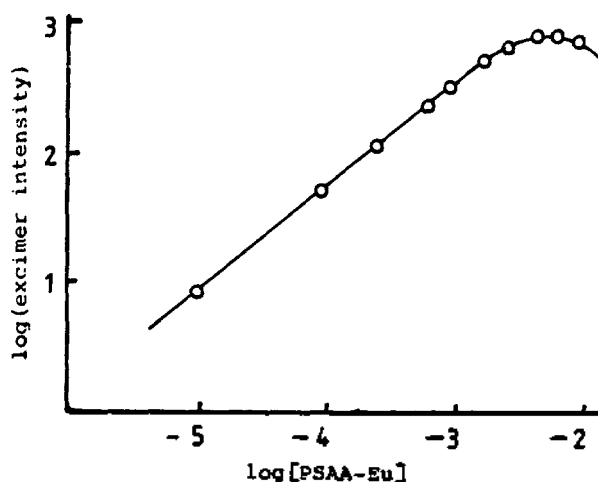


Figure 2. Fluorescence intensity of excimer of PSAA-Eu complex at 328nm as a function of the complex concentration.

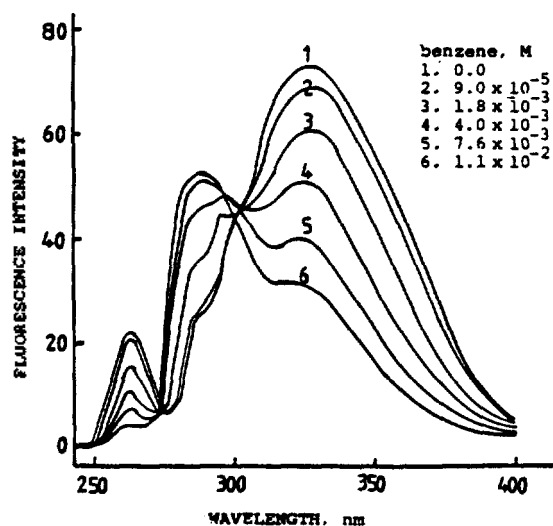


Figure 3. Fluorescence emission spectra for PSAA-Eu complex in THF depending on benzene concentration. $\lambda_{ex} = 260nm$.

the stronger emission of benzene itself at higher concentrations. The variation of the monomer intensity is feeble in the light of the decrease in intensity of the excimer. It was difficult to draw any significant conclusion from these considerations, but the decrease of the excimer intensity did not seem to result in increase of the monomer intensity. The complete understanding of the variation of monomer intensity will require a detailed study by using non-overlapping solvents other than benzene or toluene.

The addition of toluene exhibited similar effects. At low concentrations studied here, benzene and toluene molecules do not compete in absorption of energy with the aromatic groups in the polymer to reduce the excimer intensity as can be expected from Figure 2. Thus the reduction of the excimer intensity in the presence of benzene and toluene has indication of a quenching process occurring in the solution.

Stern-Volmer Plot. If benzene and toluene behave like quenchers, the excimer intensities in the absence (F_0) and presence (F) of quencher satisfy $F_0/F = 1 + k_q \tau_0 [Q]$ where k_q is the rate constant of excimer quenching, τ_0 the lifetime of excimer in the absence of quencher, and the concentration of quencher. A linear plot of F_0/F versus $[Q]$ was obtained as illustrated in Figure 4, which indicates a single class of excimers all equally accessible to quenchers. The excimer lifetime, 15nsec for polystyrene-methylmethacrylate¹⁰ and polystyrene-0.01% 2-phenyl-(5-vinyl) phenyloxalate¹¹ was adopted for that of PSAA-Eu complex to calculate k_q as a first approximation because the decay mechanism of excimer seems to be insensitive to the polymer composition when styrene is a predominant comonomer. The value of k_q was determined from Figure 4 as 8.0×10^9 and $1.7 \times 10^{10} M^{-1} S^{-1}$ for benzene and toluene, respectively. An increase in temperature from 21 to 36°C resulted in approximately 15% increase in F_0/F , which provides a supplementary evidence for the diffusive nature of the quenching.

It is informative to calculate the value expected for a diffusion-controlled reaction. The viscosity of THF at 25°C is 0.46cP¹². In the presence of $4 \times 10^{-3}M$ PSAA-Eu complex the of roughly 3Å for benzene, one can calculate from $D = kT/6\pi \eta R$ that the diffusion coefficient is $1.6 \times 10^6 cm^2/sec$. Assume radius of the excimer¹ of about 3.5Å and the diffusion of the fluorophore negligible compared to the quencher. Substitution of these values into the Smoluchowski equation¹³, $k = 4\pi RDN/1000$ where R is generally assumed to be sum of the molecular radii of fluorophore and quencher, D is sum of the diffusion

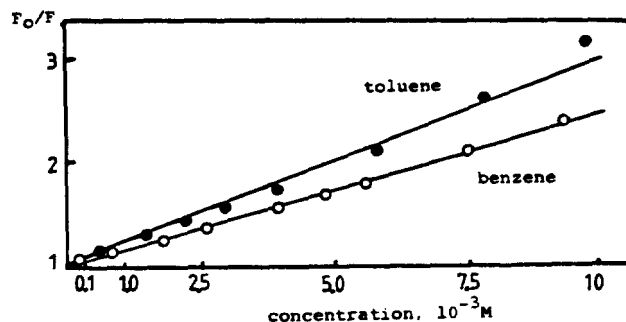


Figure 4. Quenching of the excimer fluorescence by benzene and toluene.

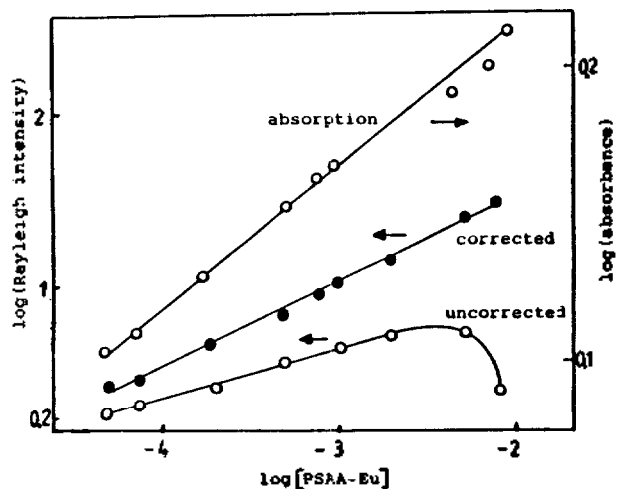


Figure 5. Absorbance and intensity of Rayleigh scattering of PSAA-Eu complex at 260nm versus the complex concentration.

coefficients of fluorophore and quencher, and N is Avogadro's number, yields $k = 7 \times 10^9 \text{M}^{-1}\text{S}^{-1}$. The magnitudes of k_q with benzene and toluene seem to be in the range of diffusion-controlled quenching since inclusion of the rapid segmental motion of the polymer would increase k assuming viscosity variation as the change in quencher concentrations is small.

Effect of Naphthalene. Data for naphthalene quenching of the excimer were not quantitatively evaluated because of severe overlap of the naphthalene emission with the excimer. However, a careful inspection of the fluorescence spectra revealed that with $5 \times 10^{-4} \text{M}$ naphthalene, the excimer emission of $4 \times 10^{-3} \text{M}$ PSAA-Eu was completely disappeared whereas the monomer emission remained fairly constant.

From these studies, the quenching efficiencies of the excimer were found to decrease in the following order: naphthalene > toluene > benzene. Presumably a bulkier quencher appears to be more efficient.

Europium Emission. The emission spectrum of PSAA-Eu complex in THF under excitation at 394nm showed peaks at 617, 595 and 700nm corresponding transitions from $5D_2$ to $7F_2$, $7F_1$, and $7F_4$ levels, respectively^{3d,14}. Among them the emission at 617nm is most intense. The fluorescence intensity increased linearly with increasing Eu contents in the complex up to about 10 wt %. For film or powder samples of PSAA-Eu, however, the intensity reaches a maximum at 4–6 wt % due to formation of ionic aggregates where metal ions are close together^{3c}. Contrary to solid samples, europium ion in the complex are apparently not so close to exhibit concentration quenching in solutions even up to 10 wt % of Eu.

Rayleigh Scattering. In dilute polymer solutions, the ratio of scattered to incident intensity has an approximate linear dependence on the polymer concentration¹⁵. When the molecular size of the polymer varies as concentration changes, the ratio is reduced by a factor of $(1 - kR_p^2)$ where k is a constant and R_p is roughly the diameter of the polymer molecule¹⁵.

Figure 5 shows the intensity of Rayleigh scattering of PSAA-Eu complex in THF at 260nm versus the complex concentration. Beyond $1.3 \times 10^{-3} \text{M}$ it deviates from linearity and decreases sharply at higher concentrations. One may suppose the decrease results from the changes of size and shape in the polymer. This

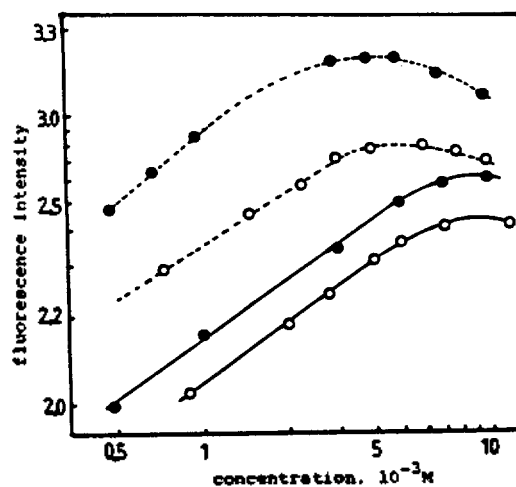


Figure 6. Fluorescence intensities of benzene (solid lines) and toluene (broken lines) in the absence (dark circles) and presence (open circles) of PSAA-Eu complex at their emission maxima versus the concentrations of benzene and toluene.

assumption turned out invalid by a simple analysis of the Rayleigh scattering in terms of absorption. Since the part of incident light absorbed by the complex does not contribute to scattering, the measured scattering intensity should be divided by a factor, e^{-A} where A is the absorbance of the complex at 260nm. As illustrated in Figure 6 the corrected Rayleigh scattering increases linearly, which implies that no structural change is measurable under the experimental conditions.

Fluorescence of Quencher. Figure 6 shows the fluorescence intensities of benzene and toluene with and without PSAA-Eu complex in THF at their emission maxima, 288 and 285nm, respectively, depending on the respective concentration. The figure demonstrates the polymer quenches the fluorescence emission of benzene and toluene as evidenced by equal downward displacement of the curves for the solutions containing the complex. At a given concentration of the complex the ratio of intensity without the complex to that with the complex should remain a constant greater than 1 for all benzene concentrations. The displacement is larger in the case of toluene, again indicating toluene has a bigger rate constant of quenching than benzene.

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References

- (1) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).
- (2) J. Roots and B. Nyström, *Eur. Polym. J.*, **15**, 1127 (1979) and references therein.
- (3) (a) P. Ander and M. K. Mahmoudhagh, *Macromolecules*, **15**, 213 (1982); (b) Y. Okamoto, Y. Ueba, I. Nagata, and E. Banks, *ibid.*, **14**, 807 (1981); (c) Y. Okamoto, Y. Ueba, N. F. Dzhanihenkov, and E. Banks, *ibid.*, **14**, 17 (1981); (d) E. Banks, Y. Okamoto, and Y. Ueba, *J. Appl. Polym. Sci.*, **25**, 359 (1980); (e) Y. Okamoto and R. Li, *Proc. IUPAC MACRO* **82**, 904 (1982).
- (4) S. I. Weissman, *J. Chem. Phys.*, **10**, 214 (1942).
- (5) S. N. Semerak and C. W. Frank, *Adv. in Polym. Sci.*, **54**, 31

- (1983).
- (6) F. S. Richardson, *Chem. Rev.*, **82**, 541 (1982).
- (7) J. R. Witt and E. I. Onstott, *J. Inorg. Nucl. Chem.*, **24**, 637 (1962).
- (8) E. Pajot-Augy, L. Bokobza, L. Monnerie, A. Castellan, H. Bouas-Laurent, and C. Millet, *Polymer*, **24**, 117 (1983).
- (9) K. Sienicki, *Polym. Bulletin*, **10**, 470 (1983).
- (10) G. Rumbles, in "Photophysics of Synthetic Polymer," Ed. by D. Phillips and A. J. Roberts, Whitstable Litho Ltd., Whitstable, England, p. 5, 1982.
- (11) A. J. Roberts, *ibid.*, p. 111.
- (12) J. A. Riddick and W. B. Bunger, "Organic Solvents," Wiley-Interscience, New York, 1970.
- (13) J. R. Lakowicz, "Principles of Fluorescence Spectroscopy", Plenum, New York, p. 262, 1983.
- (14) H. C. Kandpal and H. B. Tripathi, *Solid State Commu.*, **40**, 673 (1981).
- (15) D. Eisenberg and D. Crothers, "Physical Chemistry," Benjamin, Menlo Park, p. 635, 1979.

Comparison of *ab initio* Effective Valence Shell Hamiltonian with Semiempirical Theories of Valence: Pairing Theorem

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The pairing properties of electronic structure are investigated from *ab initio*'s point of view. Numerical results of exact *ab initio* effective valence shell Hamiltonian are compared with simple semiempirical Hamiltonian calculations. In the oxygen atom case it was found that effective three-electron interaction terms break the similarity between electron-states and hole-states. With the *trans*-butadiene as an example the pairing theorem was studied. Even for alternant hydrocarbons, the deviation from the pairing was found to be enormous. The pairing theorem, which is usually stated for semiempirical Hamiltonians, is not valid when the exact effective Hamiltonian is considered. The present study indicates that comparisons between the pairing theorem of semiempirical methods and *ab initio* effective Hamiltonian give important information on the accuracy of semiempirical methods.

Introduction

In atomic spectra elements carbon and oxygen show a similar pattern, which is probably due to the nominally same electronic structure of the two elements. It is understood with the idea of electrons and holes in the similar 2p shell.¹ Carbon has two electrons in the 2p shell, while oxygen has two holes. The positive and negative ions of an alternant hydrocarbon also exhibit a very similar spectroscopic pattern.² This remarkable phenomenon is often explained using the so called pairing theorem in molecular orbital theory. But the pairing of two spectra does not hold exactly, as McLachlan³ and Koutecký⁴ showed that the pairing is valid only under certain approximations.

Any molecules or atoms have a finite number of electrons, but infinite number of single-electron orbitals are required to exactly describe the electronic structure of the systems. Therefore a number of electrons of a system can not be same as holes of any other systems. The concept of the equalness between a number of electrons and that of holes is valid only when a finite number of orbitals are considered. Usually valence orbitals are chosen for that purpose. For alternant hydrocarbons π orbitals are often considered as valence orbitals. So it is important to note that the pairing theorem holds only for an approximate Hamiltonian which spans on a finite valence space. The well-known examples satisfying the pairing theorem are

one-electron Hückel Hamiltonian⁵ and Pariser-Parr-Pople (PPP) Hamiltonian⁶⁻⁸ with zero differential overlap approximation. It indicates that the pairing properties of electronic structure are often stated in simple semiempirical theories. The pairing has not drawn any attentions from *ab initio*'s who are always worried about extensive virtual orbitals.

Recently an *ab initio* effective valence shell Hamiltonian formalism which formally mimicks semiempirical Hamiltonians has been developed.⁹⁻¹¹ The full Hamiltonian is transformed to an effective one which spans on small valence space only, yet the transformation is performed exactly. The effective valence shell Hamiltonian is *ab initio* Hamiltonian which conveniently generates useful effective integral values amongst valence orbitals. Therefore it is now possible to examine the validity of the pairing theorem of semiempirical Hamiltonians. The purpose of the present work is to understand when the pairing theorem is valid and furthermore to assess the accuracy of approximate semiempirical methods.

Extensive calculations of the effective valence shell Hamiltonian on various atoms^{12,13} and *trans*-butadiene¹⁴ have appeared in literature. Therefore in the present work we choose oxygen atom and *trans*-butadiene as our prototype system. The valence state of oxygen atom and its doubly positive ion, O²⁺, are formally studied as an electron-hole model case. The pairing pro-