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A Theoretical Study on the Chemisorption Effects in SERS

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Received January 22, 1993

With the chemisorption theory based on the charge-transfer model, we evaluate the enhancement ratios in surface enhanced Raman scattering. The extended Hückel (EH) calculation and fragment molecular orbital (FMO) analysis have been applied to a system composed of a pyridine molecule adsorbed on a silver cluster. The calculation shows that the enhancement ratios due to the resonant metal-to-molecule charge-transfer are assessed about 1-170.

Introduction

The surface enhanced Raman scattering (SERS) phenomena due to interaction between metal surface and adsorbate molecule have been studied since the discovery of Fleischman.¹ It is now widely accepted that two separate mechanisms must be involved in the origin of SERS.²⁻⁴ The electrodynamic mechanism shows that the enhancement results from the surface plasmon resonances. The enhancement ratios of up to 10^4 can be explained by this mechanism.⁵ However, it was also realized that certain types of molecules display enhancement ratios still greater by factors of 10 to 10^3 . These are molecules such as pyridine or piperidine having a lone pair of electrons available for bonding with surface. The charge-transfer mechanism due to chemisorption was proposed by Adrian, Lippitsch and Lombardi. We focus on the effect of chemisorption in this work. The chemisorption theory has experienced an evolution. Adrian⁶ emphasized on Franck-Condon overlap integral, but ignored Herzberg-Teller term.⁷ Lippitsch⁸ included vibronic coupling of the molecular ground electronic state with states of the metal in attempt to complement Adrian's theory. Lombardi⁹ applied the Herzberg-Teller conditions to a metal-molecule system. Lombardi's theory provides plausible explanations about the intensity profile of experiments and the enhancement of non-totally symmetric mode. The goal of this work is evaluation of enhancement ratio of chemisorption origin on the basis of Lombardi's theory. To evaluate the enhancement ratio, the transition moment between states of metal and molecule, and the energy level of metal are calculated, using the vibronic coupling constants between metal and molecule, and Franck-Condon overlap integral as variables.

Method

We model pyridine-silver system as a typical case of SERS.

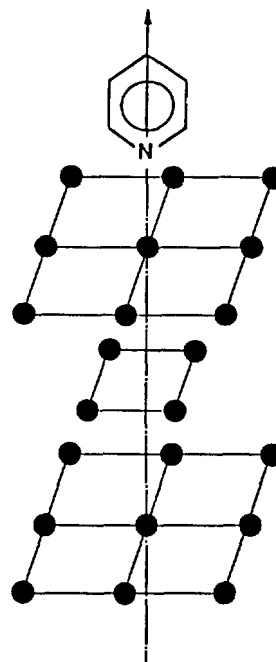


Figure 1. Pyridine-silver cluster model. The Ag_{22} cluster and pyridine have D_{4h} and C_{2v} symmetry respectively. In head-on adsorption configuration, combined system has C_{2v} symmetry.

The silver surface is represented by a cluster of three layers of 22-atoms. The cluster has been proved as a reasonable model for the calculation and for the representation of surface.¹⁰ The geometry is given in Figure 1. The Ag-Ag distance is taken as 2.89 \AA ,¹¹ which is the nearest neighbour distance in bulk silver. We take the Ag-N distance to be 2.302 \AA ,¹² which is found in an Ag complex. The EH parameters¹³ used in the calculation are collected in Table 1. The parameters for Ag are taken from the calculation of Hoff-

Table 1. Extended Hückel Parameters^d

Orbital	H_{ii} (eV)	ξ_1^b	ξ_2^b	C_1^c	C_2^c
Ag 5s	-11.10	2.244			
Ag 5p	-5.80	2.202			
Ag 4d	-14.50	6.070	2.6630	0.55910	0.60476
H 1s	-13.60	1.30			
C 2s	-21.40	1.625			
C 2p	-11.40	1.625			
N 2s	-26.0	1.950			
N 2p	-13.4	1.950			

^aR. Hoffmann, *J. Phys. Chem.*, **94**, 3046 (1990). ^bExponents in a double- ξ expansion of the metal d orbitals. ^cCoefficients in a double- ξ expansion of the metal d orbitals.

mann on the O₂ chemisorption on the Ag(110) surface.

In the case of metal-adsorbate system, the polarizability has been shown by Lombardi as follows:⁹

$$\alpha_{op} = A + B + C. \quad (1)$$

The term A is either A_f or A_k depending on the situation:

$$A_f = (2/\hbar) \sum_M M_{MI}^o M_{MI}^p \langle i|k \rangle \langle k|f \rangle \frac{\omega_{MI} + \omega_f}{(\omega_{MI} + \omega_f)^2 - \omega^2}, \quad (2)$$

$$A_k = (2/\hbar) \sum_M M_{KM}^o M_{KM}^p \langle i|k \rangle \langle k|f \rangle \frac{\omega_{KM} + \omega_k}{(\omega_{KM} + \omega_k)^2 - \omega^2}, \quad (3)$$

where ω_k and ω_f are the frequencies of a particular excited and ground state vibration respectively, I and K denote molecular electronic ground state and excited state of chemisorbed pyridine and M denotes metal states respectively. The term A_f represents molecule-to-metal charge-transfer from the molecular electronic ground state to one of the unfilled metal levels M , while A_k represents metal-to-molecule charge-transfer from a filled metal state M to an excited state K of molecule.

The term B stands for molecule-to-metal charge-transfer from molecular electronic ground state to one of the unfilled metal levels M . The term C stands for metal-to-molecule charge-transfer from one of the filled metal levels M to the excited state K of molecule.

$$B = -(2/\hbar^2) \sum_{K>I} \sum_{M>K} (M_{KI}^o M_{MI}^p + M_{KI}^p M_{MI}^o) \frac{(\omega_{KI} \omega_{MI} + \omega^2) h_{IM} \langle i|Q|f \rangle}{(\omega_{KI}^2 - \omega^2)(\omega_{MI}^2 - \omega^2)} \quad (4)$$

$$C = -(2/\hbar^2) \sum_{K>I} \sum_{M>I} (M_{MK}^o M_{KI}^p + M_{MK}^p M_{KI}^o) \frac{(\omega_{KI} \omega_{KM} + \omega^2) h_{IM} \langle i|Q|f \rangle}{(\omega_{KI}^2 - \omega^2)(\omega_{KM}^2 - \omega^2)} \quad (4)$$

The transition corresponding to the C term obtains its intensity *via* M_{MK} through intensity borrowing from the allowed $I \rightarrow K$ transition. The h_{IM} means vibronic coupling of the metal to the ground molecular level through some vibrational mode. In silver-pyridine system, metal-to-molecule charge-transfer is assumed.¹⁴ Also the resonance condition is satisfied by the metal states, which are located between HOMO and LUMO of pyridine, and LUMO of chemisorbed pyridine

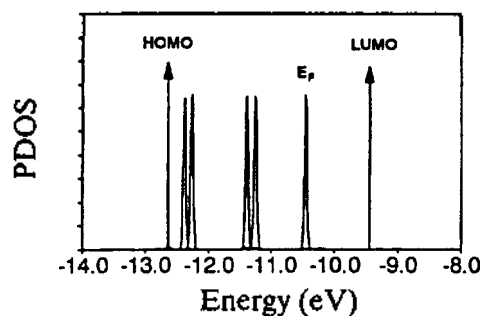


Figure 2. Projected Density of States (PDOS) of 5s from Ag₂₂-pyridine. PDOS²¹ is defined by $\rho_i(E) = (2\pi\sigma^2)^{-1/2} \sum_k |C_k|^2 \exp[-(E - e_k)^2/2\sigma^2]$. E_F denotes the fermi level of the silver cluster. The HOMO and LUMO of pyridine are given for reference. The filled 5s states near E_F are located between HOMO and LUMO of free pyridine.

(Figure 2).

Therefore, we focus an A_k and C . To simplify the mathematics, I and K are fixed to HOMO and LUMO of chemisorbed pyridine respectively, and will be defined precisely later. For the resonant metal-to-molecule charge-transfer, the Eqs. (3, 5) can be rewritten:

$$A_k = (2/\hbar) \sum_M M_{KM}^o M_{KM}^p \langle i|k \rangle \langle k|f \rangle \left| \frac{\omega_{KM} + \omega_k}{(\omega_{KM} + \omega_k - \omega + i\Gamma)(\omega_{KM} + \omega_k + \omega)} \right| = \sum_M K_{SM} K_{FM}, \quad (6)$$

$$K_{SM} = (2/\hbar) M_{KM}^o M_{KM}^p \langle i|k \rangle \langle k|f \rangle, \quad (7)$$

$$K_{FM} = \left| \frac{\omega_{KM} + \omega_k}{(\omega_{KM} + \omega_k - \omega + i\Gamma)(\omega_{KM} + \omega_k + \omega)} \right|. \quad (8)$$

$$C = -(2/\hbar^2) \sum_{M>I} [M_{MK}^p M_{KI}^o + M_{MK}^o M_{KI}^p] h_{IM} \langle i|Q|f \rangle \times \left| \frac{\omega_{KI} \omega_{KM} + \omega^2}{(\omega_{KI}^2 - \omega^2)(\omega_{KM} - \omega + i\Gamma)(\omega_{KM} + \omega)} \right| = \sum_{M>I} K_{SM} K_{FM}, \quad (9)$$

$$K_{SM} = -(2/\hbar^2) [M_{MK}^p M_{KI}^o + M_{MK}^o M_{KI}^p] h_{IM} \langle i|Q|f \rangle, \quad (10)$$

$$K_{FM} = \left| \frac{\omega_{KI} \omega_{KM} + \omega^2}{(\omega_{KI}^2 - \omega^2)(\omega_{KM} - \omega + i\Gamma)(\omega_{KM} + \omega)} \right|. \quad (11)$$

The Γ denotes the linewidth of chemisorbed pyridine. We use a linewidth parameter Γ of 0.3 eV and vibrational frequency of excited state $\omega_k = 0.2$ eV.⁹ The K_{SM} and K_{FM} terms are dependent on selection rule and laser frequency respectively.

Results and Discussion

To obtain the enhancement ratio, the polarizability of free pyridine is calculated as a reference. In the case of $\omega \ll \omega_{KI}$, B can be expressed⁷:

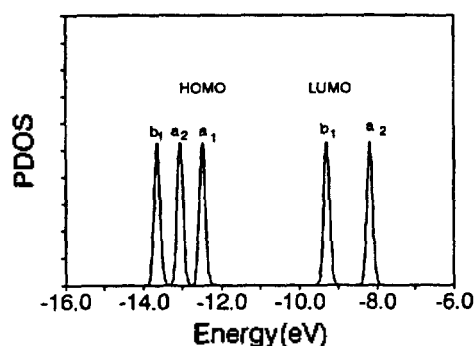


Figure 3. PDOS²¹ of free pyridine. The symmetry species of pyridine's MO are described. The $a_1 \rightarrow b_1$ and $a_2 \rightarrow b_1$ transitions correspond to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively.

$$B_o = \sum_{K \neq I} \sum_{M \neq K} K_{SM}^0 K_{FM}^0 \quad (12)$$

$$K_{SM}^0 = -(2/\hbar^2) [M_{KI}^{00} M_{MI}^{00} + M_{KI}^{00} M_{MI}^{00}] h_{KM}^0 \langle i|Q|f \rangle, \quad (13)$$

$$K_{FM}^0 = \frac{(\omega_{KI} \omega_{MI} + \omega^2)}{(\omega_{KI}^2 - \omega^2)(\omega_{MI}^2 - \omega^2)}, \quad (14)$$

where I denotes ground state of free pyridine, K and M represent excited states of free pyridine, and $h_{KM}^0 \langle i|Q|f \rangle$ denotes vibronic coupling constants in free pyridine. The superscript ⁰ means unperturbed free pyridine. Generally it is known that the electronic spectra of N-heterocyclic compounds show strong perturbations between $n\pi^*$ and $\pi\pi^*$ states.¹⁵ We assume that ${}^1B_1(n\pi^*)$ and ${}^1B_2(\pi\pi^*)$ states of pyridine are coupled by some vibrational mode. The n, π, π^* orbitals correspond to HOMO, occupied MO near HOMO, LUMO of pyridine respectively.¹⁶ Figure 3 depicts the symmetry of each MO. The B_o can be expressed as

$$I_o \propto (B_o)^2, \quad (15)$$

$$B_o \approx K_{SM}^0 K_{FM}^0, \quad (16)$$

where I_o denotes the Raman intensity of free pyridine. The selection rules of K_{SM}^0 are well known,⁷ transition moments of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ are obtained from experiment.¹⁶

The $h_{KM}^0 \langle i|Q|f \rangle$ is estimated with Eq. (16) and polarizability, which is obtained by Pariser-Parr-Pople (PPP) method.¹⁷

In the case of chemisorbed pyridine, we must consider total wavefunction which is consisted of pyridine and silver cluster functions. For isolated system the wavefunction of each fragment is expressed as

$$\phi_i^0 = \sum_{\mu} \xi_{\mu} a_{\mu i}, \quad (17)$$

$$\phi_j^0 = \sum_{\nu} \eta_{\nu} b_{\nu j}. \quad (18)$$

In Eqs. (17) and (18), $a_{\mu i}$ and $b_{\nu j}$ denote atomic coefficients of molecule and metal respectively. Then the wavefunction of combined system can be expressed:

$$\Psi_k = \sum_{\mu} \xi_{\mu} a'_{\mu k} + \sum_{\nu} \eta_{\nu} b'_{\nu k} \quad (19)$$

$$= \sum_i \phi_i^0 a_{ik} + \sum_j \phi_j^0 \beta_{jk} \quad (20)$$

where $a'_{\mu k}$ and $b'_{\nu k}$ denote atomic orbital coefficients of mole-

Table 2. Values of K_{SM} (unit in parenthesis)

	M (Å)	M (Å)	$[h \langle i Q k \rangle]^2$ (cm ⁻¹)	$\langle i k \rangle \langle k f \rangle$
K_{SM} of Eq. (13)	0.089 ^a	0.27 ^b	241 ^d	
K_{SM} of Eq. (7)	0.041 ^c	0.041 ^c		$f(r)^e$
K_{SM} of Eq. (10)	0.089 ^a	0.041 ^c	$t^2 \cdot 241^f$	

^aThe transition moment of $n \rightarrow \pi^*$ in free pyridine. ^bThe transition moment of $\pi \rightarrow \pi^*$ in free pyridine. ^cThe transition moment between MO of 5s state and LUMO of pyridine. ^dVibronic coupling constant of free pyridine. ^e $f(r) \equiv e^{-r^2} (r^2 - k) r^{2k-1} / k!$ (for $\Delta v = 1$) (See text.). ^fVibronic coupling constant of pyridine in combined system, the parameter of vibronic coupling constant, $t = [h_{FM} / h_{KM}^0]$ (See text.).

cule and metal in combined system respectively. α_{ik} and β_{jk} denote the molecular orbital coefficients of fragments such as molecule and metal respectively. This total wavefunction can not be used in Eqs. (6)-(11), in which the wavefunctions require identity of each fragment (metal, molecule). Therefore we define the following wavefunctions:

$$\phi_i^{mol} = \sum_k \langle \phi_i^0 | \Psi_k^{mol} \rangle \cdot | \phi_i^0 \rangle, \quad (21)$$

$$\phi_j^{met} = \sum_k \langle \phi_j^0 | \Psi_k^{mol} \rangle \cdot | \phi_j^0 \rangle, \quad (22)$$

which are perturbed functions due to chemisorption. Substituting Eq. (20) into Eqs. (21, 22), we obtain

$$\phi_i^{mol} = \sum_k (\alpha_{ik} + \sum_j S_{ij} \beta_{jk}) \cdot | \phi_i^0 \rangle, \quad (23)$$

$$\phi_j^{met} = \sum_k (\beta_{jk} + \sum_i S_{ij} \alpha_{ik}) \cdot | \phi_j^0 \rangle, \quad (24)$$

$$S_{ij} = \langle \phi_i^0 | \phi_j^0 \rangle. \quad (25)$$

Generally the interaction between pyridine and silver surface is weak.¹⁸ Since the overlap integral (S_{ij}) of Eq. (25) can be ignored in Eqs. (23, 24), the wavefunctions are expressed:

$$\phi_i^{mol} = \sum_k \alpha_{ik} | \phi_i^0 \rangle, \quad (26)$$

$$\phi_j^{met} = \sum_k \beta_{jk} | \phi_j^0 \rangle. \quad (27)$$

These wavefunctions are given by fragment molecular orbital (FMO) analysis. With wavefunctions of Eqs. (26, 27) we can consider the split and shift of energy levels due to chemisorption. The selection rule terms of Eqs. (7, 10) are evaluated by assuming that the symmetry of fragment wavefunction is equivalent to that of total wavefunction.

The transition moment M_{KM} is defined by

$$M_{KM} = \langle K | \mu_0 | M \rangle, \quad (28)$$

where K and M denote the LUMO of pyridine and the 5s states of metal silver in combined system respectively. Eq. (28) can be rewritten by assuming that $\alpha_{ik} = 1$ only when $k = k'$, $\beta_{jk} = 1$ only when $k = k''$ otherwise $\alpha_{ik} = \beta_{jk} = 0$ in Eqs. (26, 27) as follows:

$$M_{KM} = \langle \phi_i^0 | \mu_0 | \phi_j^0 \rangle. \quad (29)$$

If one adopts adatom model, silver may be approximated by one silver atom, and then Eq. (29) can be estimated (Ta-

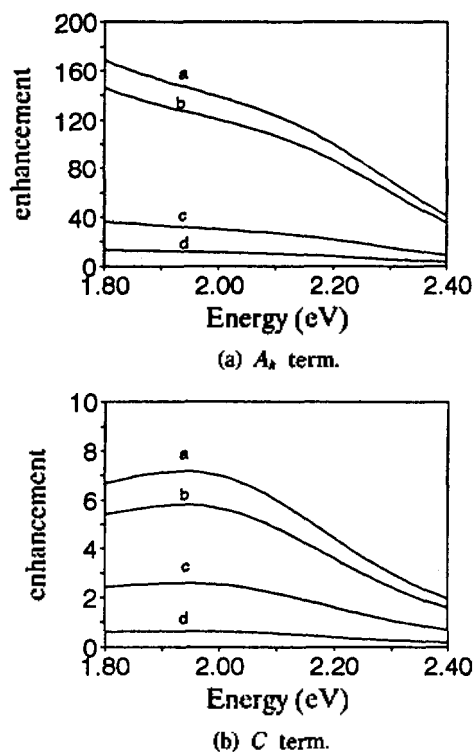


Figure 4. Enhancement due to chemisorption. (a) A_s term. The lines of a , b , c and d correspond to $r=0.6, 0.3, 1.2$ and 0.9 respectively. The enhancement ratios are expressed as a function of laser frequency for various r values. The enhancement ratios, resulted from the fulfillment of resonance Raman condition, are about 1-170 depending upon r values. (b) C term. The lines of a , b , c and d correspond to $t=1.0, 0.9, 0.6$ and 0.3 respectively. The enhancement ratios are given as a function of laser frequency for various t values. The enhancement ratios, resulted from the fulfillment of resonance Raman condition, are about 1-8 depending upon t values.

ble 2). The selection rule of $\langle i|k\rangle \langle k|f\rangle$ in Eq. (7) is well established,⁷ and allows the intensity of totally-symmetric mode.⁹ The magnitude can be expressed by assuming that the fundamental transition⁶ as following:

$$\langle i|k\rangle \langle k|f\rangle = e^{-r^2} (r^2 - k) r^{2k-1} / k! \quad (30)$$

where $r = \delta Q_k / 2\langle Q_k \rangle$, $\langle Q_k \rangle = (\hbar / 2\mu_k \omega_k)^{1/2}$. Here δQ_k is the change in the origin of the k th vibrational mode due to the change in nuclear equilibrium position on going from the ground to the excited electronic states, and $\langle Q_k \rangle$ is the root-mean-square vibrational displacement of the k th mode in the ground state, where μ_k and ω_k are the reduced mass and frequency for the k th mode respectively. We evaluate the vibrational overlap integral in the range of $0 < r < 1.2$.⁵

In Eq. (10) the vibronic coupling element $\hbar_{IM} \langle i|Q|f\rangle$, which allows the intensity of non-totally symmetric mode,⁹ plays an important role in metal-to-molecule charge-transfer. We assume that the $\langle i|Q|f\rangle$ is identical in isolated and combined system. Magnitude of \hbar_{IM} may be dependent on the overlap integral between HOMO of pyridine and MO of silver.⁸ To obtain enhancement between free and chemisorbed pyridine, the ratio between \hbar_{IM} and \hbar_{KM}^0 may be taken as a variable:

$$t = [|\hbar_{IM} / \hbar_{KM}^0|] \quad (31)$$

If we take \hbar_{KM}^0 as constant, then the variable t may be proportional to the overlap $\langle I|M\rangle$. If we assume the weak chemical bonding of pyridine and silver, it seems reasonable to estimate t as $0 < t < 1$.

With Eqs. (6, 9) and Eq. (16) the enhancement ratios, intensity ratios of chemisorbed pyridine to free pyridine, are evaluated using r in A_s and t in C as variables. We express the enhancement ratios as a function of laser frequency ω and display in the range of $1.8 \text{ eV} < \omega < 2.4 \text{ eV}$ (Figure 4), which corresponds to the frequency range of laser used in SERS. We obtain the enhancement of totally symmetric mode from A_s , 1-170, and non-totally symmetric mode from C , 1-8 depending upon r and t respectively. These values roughly agree with experimental results¹⁹ of 15-65. The intensity ratio of totally symmetric mode to non-totally symmetric mode is about 1-25, which agrees with experimental result.²⁰

The existence of t in C term implies that the strength of chemical bonding between silver cluster and pyridine is related to Raman intensity.

Conclusion

With the chemisorption theory based on charge-transfer model, we obtain the following results:

- (1) The new energy levels resulted from vibronic coupling between pyridine and silver cluster satisfy the resonance Raman condition.
- (2) The resonance condition gives the enhancement of 1-170 for totally symmetric mode, 1-8 for non-totally symmetric mode.
- (3) The fact that the intensity of totally symmetric mode is larger than that of non-totally symmetric mode agrees with experimental result of SERS.

Acknowledgement. This work has been supported by the Ministry of Educations, S.N.U. Daewoo Research Fund and Korea Science and Engineering Foundation.

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Micellization of Dodecyltrimethylammonium Bromide in D₂O as Probed by Proton Longitudinal Magnetic Relaxation and Chemical Shift Measurements

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Received February 19, 1993

¹H-NMR chemical shifts and relaxation rates of dodecyltrimethylammonium bromide (DTAB) were measured in aqueous solutions as a function of solute concentrations. Downfield chemical shifts were found on micellization for all protons. Critical micelle concentration (CMC), aggregation number (*n*), equilibrium constant (*K*) and chemical shifts of monomer and micelle (δ_{mono} , δ_{mic}) were obtained from chemical shifts measurement. In spherical DTAB micelle which is confirmed by the calculated value of surface area, the hydrocarbon chain had two gauche connections in opposite directions in average. When micelles were formed the relaxation rates of all protons were greatly increased, as their environment changed from water to liquid hydrocarbon. The variation of relaxation rates indicate that 1) part of the surfactants molecules in the micelles, *i.e.*, the head groups, are exposed to the water, 2) molecular motion in the micellar state is more restricted than in monomer state and 3) the penetration of the water molecules into micelle interior reach to the α position. A deformation from spherical to ellipsoidal micelles has been suggested for DTAB when the surfactant concentration is higher than 32.0 mM. An explanation of this possibility is given.

Introduction

Amphipathic molecules those possessing clearly defined regions of both hydrophobic and hydrophilic character are well known to form a variety of structures in an aqueous environment in which the hydrophilic moiety is exposed to the solvent and the hydrophobic one is hidden from it. These include spherical micelles, ellipsoidal micelles, rod-shaped micelles, and a variety of smectic mesophases including bilayers, vesicles, liposomes, and lamellaphase. Micelle formations of a surfactants in solution is induced by the hydrophobic interaction between hydrocarbon parts of the surfactant molecules balanced by their hydration and electrostatic repulsive effects. A micelle is formed cooperatively at CMC¹, which is characteristic of the surfactant species and that CMC is usually influenced by various factors such as temperature and ionic strength. If the length of the hydrophobic chain is increased, the hydrophobic effect becomes more strong and, consequently, the CMC decreases and larger micelles are formed.^{2,3} Such micelle structures derived from sim-

ple surfactant molecules serve as both structural and functional models for more complex ones, including proteins and biomembranes, constructed from the correspondingly more complex biological surfactants, particularly phospholipids and cholesterol.⁴

DTAB¹ is one of the cationic surfactant which has been extensively studied by physicochemical methods. Aqueous DTAB solutions show a considerable complexity in many properties and, in particular its rather high CMC (15.0-16.0 mM)⁵⁻⁷ and sufficiently long alkyl chain length is suitable to the studies of common characters of various micelles. It is evident that the origin of the complexity of DTAB solutions, as it is expressed in the various physicochemical properties, has to be sought in various structural changes of the aggregates formed. In turn, aggregated shapes and aggregation process have to be traced back to the different types of interactions at the molecular level, *i.e.*, surfactant-surfactant, surfactant-water, surfactant-counterion, surfactant-solubilisate, etc. In order to study the highly specific effect on aggregate structures and processes in aqueous DTAB so-