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Crystal Structure of Cholesteryl Methyl Ether

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Received February 8, 1989

Cholesteryl methyl ether($CH_3OC_{27}H_{45}$) crystallizes in the monoclinic space group $P2_1$ with a = 11.740 (8), b = 7.576 (5), c = 15.492 (10)Å, β = 110.39 (5)°, Z = 2, Dc = 1.03 g/cm^3 and Do = 0.96 g/cm^3. The intensities were collected on a Nonius CAD-4 diffractometer with Nb-filtered Mo-K_α radiation. The structure was solved by direct methods and refined by full matrix least-squares methods. The final R factor was 0.085 for 1479 observed reflections. Compared with other cholesterol derivatives, the cholesteryl ring and tail region of the molecule are normal. The molecular long axes are parallel to the [101] axis and molecules are packed together in a similar way to those in cholesteryl chloride and bromide.

Introduction

Cholesterol is the major sterol in animal tissues. Cholesterol and its esters with fatty acids are important components of plasma lipoproteins and outer cell membrane. Cholesterol derivatives are important constituents of pathological conditions such as atherosclerosis, the formation of thick deposits of cholesterol and its esters on the inner surfaces of blood vessels, and the factors that determine their mode of crystallization and packing may be useful in understanding their deposition in arteries. In addition, the allowable tail conformations will help define permissible interactions with membrane constituents such as phospholipids.[1,2]

Although the conformation of the nucleus of cholesterol has been well established by a number of structure determinations, there are still several reasons for solving the structures of cholesterol derivatives. Though the crystal structures of many cholesterol ester derivatives[3-17] were solved, the structure of a cholesterol ether derivative has not yet been reported.

From consideration of the crystal data of the cholesteryl methyl ether, the molecules are showing a tendency to pack together in a different way to those found in other cholesterol esters. In order to investigate the structural characteristics, bond distances, bond angles, torsion angles of rings and side chain, packing mode and intermolecular interactions, the structure analysis of the cholesteryl methyl ether has been undertaken.

Experimental

Cholesteryl methyl ether was obtained from Sigma Chemical Company. Colorless prismatic crystals having their longest dimension in the b-axis direction were grown by slow evaporation of a saturated aceton solution. Oscillation and Weissenberg photographs, which showed systematic absent reflections for $0k0$ when k is odd, indicated that crystals are monoclinic with space group $P2_1$. The X-ray intensity data were measured on the Nonius CAD-4 diffractometer with Nb-filtered Mo-K_α radiation (λ = 0.7107Å). A cystal having dimensions of 0.3 mm × 0.8 mm × 0.5 mm was used in the experiment. The approximate unit cell parameters which were obtained from low angle reflections agreed with those reported earlier by Bernal, Crowfoot and Frankuchen[3]; a = 1.72, b = 7.58, c = 22.40 Å, β = 139.7°. However, this unit cell was so oblique that a new unit cell was chosen. The unit cell parameters were determined by a least-squares fit of 2θ angles for 33 reflections (14° < θ < 18°).

Detailed crystal data are as follows. $C_{28}H_{48}O$; mol. wt. 400.7; space group, monoclic, $P2_1$; z = 2; a = 11.740 (8), b = 7.576 (5), c = 15.492 (10) Å, β = 110.39 (5)°, V = 1291.47 Å^3; μ(Mo-K_α) = 0.64 cm^{-1}; D_c = 1.03 g/cm^3, D_m = 0.96 g/cm^3 measured by floatation method in a mixture of water and isopropyl alcohol. The intensity data were collected with Nb-filtered Mo-K_α radiation using the $\theta/2\theta$ scan techniques. The intensities of three reflections ($\bar{1}04$, 500, 020) were monitored every 30 reflections throughout the data collection and showed no systematic variations. The 4013 independent reflections were measured, range of hkl: $-15 \le h \le 15, 0 \le k \le 10$ and $0 \le l \le 20$, within $2° \le 2\theta \le 60°$.

Table 1. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Factors ($Å^2 \times 10^3$) for the Nonhydrogen Atoms of Cholesteryl Methyl Ether. The Estimated Standard Deviations are in Parentheses

Atom	Ueq. = $1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$			Ueq.
	x	y	z	
C(1)	4626(8)	2598(20)	7733(6)	76
C(2)	4231(9)	2633(21)	8584(6)	82
C(3)	3994(10)	807(22)	8838(7)	88
C(4)	5054(9)	-377(23)	8998(6)	93
C(5)	5550(8)	-383(21)	8205(6)	69
C(6)	5752(10)	-1846(20)	7843(7)	79
C(7)	6225(9)	-2051(20)	7079(7)	80
C(8)	6749(7)	-314(21)	6869(5)	61
C(9)	5907(7)	1262(20)	6886(6)	57
C(10)	5737(8)	1466(20)	7842(6)	59
C(11)	6278(9)	2964(19)	6541(6)	75
C(12)	6529(9)	2795(20)	5637(7)	82
C(13)	7406(7)	1303(19)	5646(6)	55
C(14)	6880(7)	-347(20)	5919(5)	57
C(15)	7630(9)	-1873(19)	5738(7)	78
C(16)	7885(9)	-1252(20)	4871(6)	77
C(17)	7455(8)	714(20)	4686(6)	62
C(18)	8684(8)	1739(21)	6317(6)	79
C(19)	6873(9)	2293(22)	8549(7)	98
C(20)	8204(8)	1801(22)	4236(6)	72
C(21)	7908(9)	3767(22)	4127(7)	87
C(22)	8101(8)	967(21)	3312(6)	77
C(23)	9056(8)	1547(22)	2915(6)	85
C(24)	8947(8)	632(22)	2024(7)	84
C(25)	10020(11)	964(25)	1697(8)	106
C(26)	9979(10)	-263(28)	910(8)	127
C(27)	10074(13)	2784(28)	1415(8)	133
C(28)	2602(11)	1402(28)	9615(8)	136
O	3677(7)	727(19)	9646(5)	107

*Lists of structure factors, anisotropic thermal parameters and atomic coordinates of hydrogen atoms are available from the author (YJP).

Structure Determination and Refinement

The structure amplitudes were converted into the normalized structure factors. Attempts to determine the structure with the program MULTAN[18] and SHELX-76[19] had been failed. The phase problem was finally solved by direct methods using the program SHELXS-86[20] using 180 reflections with $E>1.48$. The twenty peaks selected from the E map were consistent with a chemically reasonable tetracyclic ring of the cholesterol fragment. Structure factor calculation based on 20 atoms gave an R value of 0.32 for 648 reflections with $F>4\sigma(F)$. The remaining nonhydrogen atoms were located from a subsequent Fourier map.

The refinement was carried out by the full matrix least-squares method using the program SHELX-76. Four cycles of isotropic full matrix least-squares refinements lowered the R value ($R = \Sigma|Fo-Fc|/\Sigma(Fo)$) from 0.32 to 0.12 for 987 reflections with $F>3\sigma(F)$. Most of hydrogen atoms could be identified in the difference Fourier map calculated after anisotropic refinements with nonhydrogen atoms. The positions of the unidentified hydrogen atoms were calculated with ideal geometry (C-H = 1.08 Å and ∠H-C-H = 109°). The isotropic temperature factors of all hydrogen atoms were fixed to be 0.05 $Å^2$. The final R value were 0.085 for the 1479 observed reflections with $|F|>1.5\sigma(F)$. A ratio of maximum least-squares shift to error was 0.29. The weighted R value $Rw = \Sigma(w||Fo|-|Fc||)/\Sigma(w|Fo|)$ was 0.092, where $w = 0.322/(\sigma^2(Fo) + 0.001\ Fo^2)$. Atomic scattering factors were from the International Tables of X-ray Crystallography.[21] The final atomic parameters for the nonhydrogen atoms are given in Table 1.*

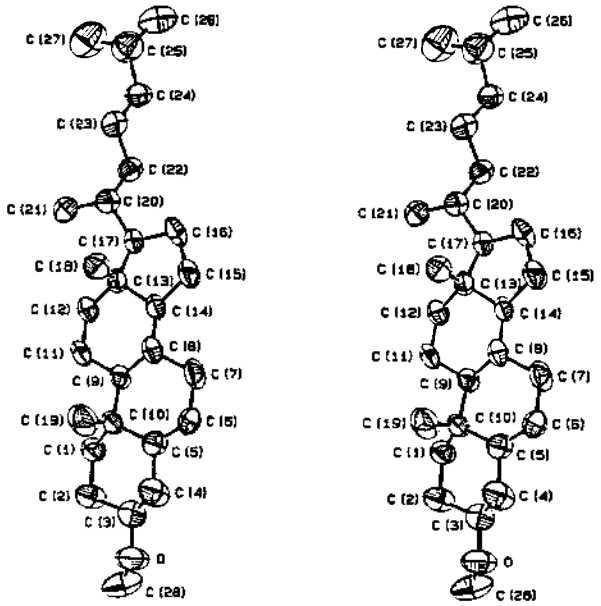

Figure 1. Molecular conformation with atomic numbering.

Results and Discussion

A stereoscopic ORTEP[22] drawing of the molecule with atomic numbering scheme is shown in Figure 1. The bond distances and angles of cholesteryl methyl ether are listed in Table 2. Bond distances and angles are in agreement with those of other cholesterol compounds[1-17] within experimen-

Table 2. Bond Lengths (Å) and Angles (°) for Cholesteryl Methyl ether. The Estimated Standard Deviations are in Parentheses

C(1)-C(2)	1.54(1)	C(1)-C(10)	1.52(1)
C(2)-C(3)	1.49(2)	C(3)-C(4)	1.48(1)
C(3)-O	1.43(1)	C(4)-C(5)	1.53(1)
C(5)-C(6)	1.30(1)	C(5)-C(10)	1.55(1)
C(6)-C(7)	1.48(1)	C(7)-C(8)	1.54(1)
C(8)-C(9)	1.56(1)	C(8)-C(14)	1.53(1)
C(9)-C(10)	1.57(1)	C(9)-C(11)	1.52(1)
C(10)-C(19)	1.53(1)	C(11)-C(12)	1.53(1)
C(12)-C(13)	1.53(1)	C(13)-C(14)	1.52(1)
C(13)-C(17)	1.57(1)	C(13)-C(18)	1.53(1)
C(14)-C(15)	1.54(1)	C(15)-C(16)	1.55(1)
C(16)-C(17)	1.57(1)	C(17)-C(20)	1.54(1)
C(20)-C(21)	1.53(1)	C(20)-C(22)	1.53(1)

C(22)–C(23)	1.52(1)	C(23)–C(24)	1.51(1)
C(24)–C(25)	1.53(1)	C(25)–C(26)	1.52(2)
C(25)–C(27)	1.45(2)	C(28)–O	1.35(1)
C(3)–C(2)–C(1)	110.5(8)	C(4)–C(3)–C(2)	112.5(9)
C(5)–C(4)–C(3)	113.5(8)	C(5)–C(10)–C(1)	109.0(7)
C(6)–C(5)–C(4)	121.7(10)	C(7)–C(6)–C(5)	127.6(9)
C(8)–C(7)–C(6)	111.7(8)	C(9)–C(8)–C(7)	110.5(6)
C(9)–C(10)–C(1)	109.6(7)	C(9)–C(10)–C(5)	109.4(7)
C(10)–C(1)–C(2)	114.6(7)	C(10)–C(5)–C(4)	115.4(9)
C(10)–C(5)–C(6)	122.9(7)	C(10)–C(9)–C(8)	112.5(9)
C(11)–C(9)–C(8)	112.6(7)	C(11)–C(9)–C(10)	113.3(7)
C(12)–C(11)–C(9)	114.9(7)	C(13)–C(12)–C(11)	113.4(8)
C(13)–C(14)–C(8)	116.1(7)	C(14)–C(8)–C(7)	111.8(7)
C(14)–C(8)–C(9)	107.8(7)	C(14)–C(13)–C(12)	105.9(6)
C(15)–C(14)–C(8)	116.3(7)	C(15)–C(14)–C(13)	104.7(6)
C(16)–C(15)–C(14)	103.1(7)	C(16)–C(17)–C(13)	102.2(7)
C(17)–C(13)–C(12)	116.6(7)	C(17)–C(13)–C(14)	100.5(6)
C(17)–C(16)–C(15)	107.5(7)	C(18)–C(13)–C(12)	110.1(7)
C(18)–C(13)–C(14)	112.7(7)	C(18)–C(13)–C(17)	110.6(7)
C(19)–C(10)–C(1)	110.4(8)	C(19)–C(10)–C(5)	107.9(8)
C(19)–C(10)–C(9)	110.4(7)	C(20)–C(17)–C(13)	119.5(7)
C(20)–C(17)–C(16)	113.1(8)	C(21)–C(20)–C(17)	115.4(8)
C(22)–C(20)–C(17)	109.4(8)	C(22)–C(20)–C(21)	111.0(9)
C(23)–C(22)–C(20)	115.5(8)	C(24)–C(23)–C(22)	113.4(8)
C(25)–C(24)–C(23)	114.1(8)	C(26)–C(25)–C(24)	111.4(10)
C(27)–C(25)–C(24)	112.4(12)	C(27)–C(25)–C(26)	109.4(11)
C(28)–O–C(3)	118.7(9)	O–C(3)–C(2)	113.7(9)
O–C(3)–C(4)	106.8(9)		

tal error. However, critical comparison is somewhat meaningless due to limited accuracy of the present study which was originated from the weakly diffracting power of the crystal. The estimated standard deviations in bond distances and angles are in the ranges of 0.01 to 0.02 Å and 0.6 to 1.2°, respectively. The bond distances in the tail portion show an apparent shortening which is characteristically observed in the crystal structures of the cholesterol derivatives and may be due to the high thermal motions. In the present structure, the C(25)–C(27) (1.45(2) Å) and C(3)–O bond (1.35(1) Å) are especially short.

Table 3. Selected Torsion Angles (°) and Asymmetry Parameters in Cholesteryl Methyl Ether. The Estimated Standard Deviations are in Parentheses

(1) Steroid skeleton			
Ring A			
C(10)–C(1)–C(2)–C(3)	−57		
C(1)–C(2)–C(3)–C(4)	56		
C(2)–C(3)–C(4)–C(5)	−52		
C(3)–C(4)–C(5)–C(10)	47		
C(4)–C(5)–C(10)–C(1)	−45		
C(2)–C(1)–C(10)–C(5)	50		
$\Delta C_s(1)$* = 7.8		$\Delta C_2(1\text{–}2)$* = 6.5	
$\Delta C_s(2)$ = 1.9		$\Delta C_2(2\text{–}3)$ = 3.8	
$\Delta C_s(3)$ = 1.9		$\Delta C_2(3\text{–}4)$ = 10.2	
Ring B			
C(10)–C(5)–C(6)–C(7)	3		
C(5)–C(6)–C(7)–C(8)	13		
C(6)–C(7)–C(8)–C(9)	−42		
C(7)–C(8)–C(9)–C(10)	59		
C(8)–C(9)–C(10)–C(5)	−43		
C(6)–C(5)–C(10)–C(9)	12		
$\Delta C_s(5)$ = 21.4		$\Delta C_2(5\text{–}6)$ = 0.6	
$\Delta C_s(6)$ = 22.0		$\Delta C_2(6\text{–}7)$ = 46.2	
$\Delta C_s(7)$ = 43.3		$\Delta C_2(7\text{–}8)$ = 46.0	
Ring C			
C(14)–C(8)–C(9)–C(11)	−49		
C(8)–C(9)–C(11)–C(12)	47		
C(9)–C(11)–C(12)–C(13)	−51		
C(11)–C(12)–C(13)–C(14)	54		
C(12)–C(13)–C(14)–C(8)	−61		
C(9)–C(8)–C(14)–C(13)	59		
$\Delta C_s(8)$ = 10.0		$\Delta C_2(8\text{–}9)$ = 11.0	
$\Delta C_s(9)$ = 6.4		$\Delta C_2(9\text{–}11)$ = 4.0	
$\Delta C_s(11)$ = 3.7		$\Delta C_2(11\text{–}12)$ = 8.7	
Ring D			
C(17)–C(13)–C(1)–C(15)	47		
C(13)–C(14)–C(15)–C(16)	−35		
C(14)–C(15)–C(16)–C(17)	9		
C(15)–C(16)–C(17)–C(13)	19		
C(14)–C(13)–C(17)–C(16)	−40		
$\Delta C_s(13)$ = 12.5		$\Delta C_2(13\text{–}14)$ = 8.1	
$\Delta C_s(14)$ = 23.7		$\Delta C_2(14\text{–}15)$ = 50.0	
$\Delta C_s(15)$ = 50.7		$\Delta C_2(15\text{–}16)$ = 72.8	
$\Delta C_s(16)$ = 56.7		$\Delta C_2(16\text{–}17)$ = 58.4	
$\Delta C_s(17)$ = 42.4		$\Delta C_2(17\text{–}13)$ = 37.0	
(2) Chain			
C(1)–C(2)–C(3)–O	177		
O–C(3)–C(4)–C(5)	−178		
C(2)–C(3)–O–C(28)	68		
C(4)–C(3)–O–C(28)	−167		
(3) Tail			
C(13)–C(17)–C(20)–C(21)	−54		
C(13)–C(17)–C(20)–C(22)	−180		
C(16)–C(17)–C(20)–C(21)	−174		
C(16)–C(17)–C(20)–C(22)	60		
C(17)–C(20)–C(22)–C(23)	−163		
C(21)–C(20)–C(22)–C(23)	68		
C(20)–C(22)–C(23)–C(24)	178		
C(22)–C(23)–C(24)–C(25)	−170		
C(23)–C(24)–C(25)–C(26)	169		
C(23)–C(24)–C(25)–C(27)	−68		

* ΔC_s: mirror plane asymmetry parameter

$$\Delta C_s = \left[\sum_{i=1}^{m} (\phi_i + \phi_i')^2/m\right]^{\frac{1}{2}}$$

ΔC_2: twofold asymmetry parameter

$$\Delta C_2 = \left[\sum_{i=1}^{m} (\phi_i - \phi_i')^2/m\right]^{\frac{1}{2}}$$

where $\Delta C_s(n)$ is a measure of the deviations from mirror symmetry about a plane passing through atom n and the diametrically opposed atom o, and $\Delta C_2(n\text{–}o)$ is a measure of the deviations from twofold symmetry about an axis bisecting bond$(n\text{–}o)$. The symmetry related torsion angles are ϕ_i and ϕ_i', and m is the number of such pairs.

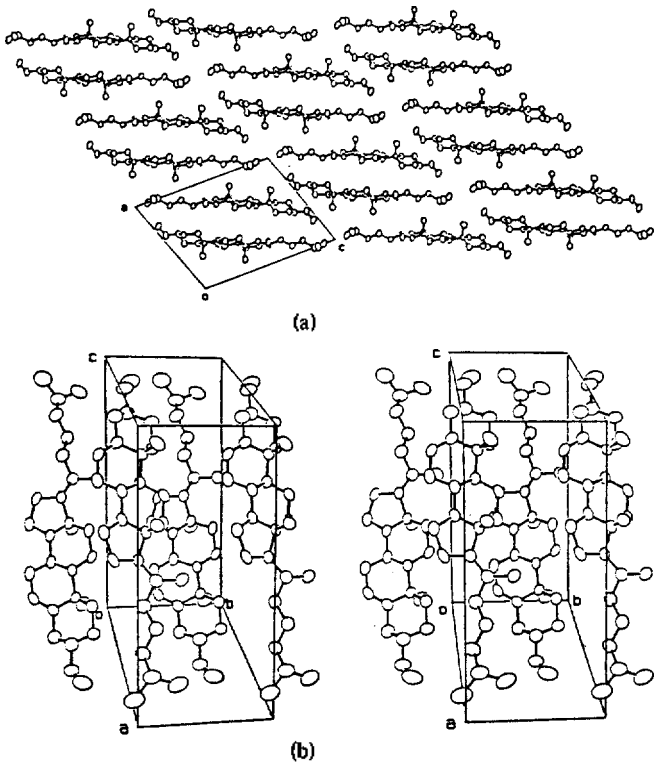

Figure 2. (a) Molecular packing in cholesteryl methyl ether viewed down the *a* axis. (b) Molecular packing in cholesteryl methyl ether viewed down the *b* axis.

The effective steroid length, represented by the C(3)---C (16) distance, is 8.98(1) Å for cholesteryl methyl ether. The C(19)–C(10)---C(13)–C(18) torsion angle, which is a measure of the twist within the ring system is 11.5(9)°. In related structures, the torsion angle ranges from 7.9 to 15.0° and the effective steroid length ranges from 8.86 to 9.01 Å.[4] Selected torsion angles and asymmetry parameters for the ring system are listed in Table 3. The mirror plane (ΔC_s) and two-fold (ΔC_2) asymmetry parameters of the ring are as defined by Duax and Norton.[23] In a perfectly symmetric saturated ring in the chair conformation, six asymmetry parameters (three rotations and three mirrors) would have magnitudes of zero, while ideal half chair conformation having only one two-fold asymmetry parameter of zero magnitude. Therfore rings A and C assume a chair conformation: for ring A, $<\Delta C_s>$ = 5.4 and $<\Delta C_2>$ = 6.8; for ring C, $<\Delta C_s>$ = 6.7 and $<\Delta C_2>$ = 7.9. Ring B assumes a half chair and ring D the expected 13β, 14α-half chair conformations.

The oxygen atom at C(3) is approximately in the cholesterol ring system and thus increases the total molecular length. The methoxy methyl C(28) is directed to the face with the torsion angle C(2)–C(3)–O–C(28) of 68.4°. The side chain at C(17) is almost fully extended. The seven atoms of C(17), C(20), C(22)---C(26) are in a zigzag planer chain and C(21) and C(27) are out of the plane. The least-squares plane of the steroid nucleus (C(1) to C(17) atoms) makes angles of 50.4° with the ether group and of 135.3° with the plane of C(17) side chain atoms.

The ORTEP packing diagrams are shown in Figure 2a and 2b. The molecules are stacked in clearly separated layers parallel to the (101) plane. The adjacent molecules in a layers are related by the 2_1 screw axis and are therefore oriented antiparallel to each other. Within each layer, the molecules are aligned with parallel cholesteryl ring systems, giving rise to a smectic type of packing. Cholesteryl C(17) tails are more loosely packed in an interface region between layers. The atoms in this part of the structure have high mean squares amplitudes of thermal vibration. Similar packing arrangements are observed in cholesteryl chloride and bromide[5] and in steroid structures[23] with two molecules per unit cell. In the cholesteryl methyl ether, the molecular long axes are parallel to the[101]axis and there is no overlap of the cholesteryl rings within one unit cell as shown in Figure 2b. There are no significantly short intermolecular contacts, and only four intermolecular contacts less than 4.0 Å, of which the shortest is C(26)---C(28) distance of 3.81 Å.

Acknowledgement. We are very grateful for the financial support by the Ministry of Education as a Free Research Project in 1987.

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Surface Tentiometric Studies on the Interaction of Anionic Polyelectrolytes with Cationic Surfactants

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The interaction of cationic surfactants, *n*-alkyltrimethylammonium bromide (C_nTAB; n = 12, 14, 16) with anionic polyelectrolyte, poly(styrenesulfonate) (PSS) has been studied by surface tension measurement. In the absence of added salt, the cationic surfactants bind to PSS quantitatively up to ca. 60% coverage of anionic sites of the polyanion and the complexes were surface inactive. Further binding of the surfactant cations on PSS caused a sharp conformational transition of the surfactant/PSS complexes to surface active complexes and accompanied precipitation. The binding showed a biphasic behavior in the presence of NaCl and cooperativity of the binding became less as the concentration of NaCl increased. Binding of the cationic surfactants on poly(vinylsulfonate) also showed the biphasic behavior and the cooperativity of the binding was much less even in the absence of NaCl. The binding of surfactant to PSS provided hydrophobic environment to solubilized pyrene and reduced the viscosity of the solution greatly even at surfactant concentrations well below cmc. This study indicated that the surfactant bound to PSS up to 60% coverage of PSS sites are present as surfactant aggregates which are wrapped up with PSS chains, and hydrophobic interaction is an important factor in the binding of the surfactants to PSS.

Introduction

The interaction between polymers and surfactants is of great interest from the fundamental standpoint of obtaining informations on the nature of the polymer/surfactant aggregates, and also from the point of practical uses of the systems in which polymers and surfactants are utilized conjointly.[1] Extensive works have been performed on polymer/surfactant systems using a variety of technigues.[2-22] From these studies, it has been found that strength of binding of ionic surfactants on dissolved polymers depends strongly on properties of the polymers and the surfactants.

Most of works on the polymer-surfactant interaction have been conducted with neutral polymers. These include poly(ethylene oxide),[2-9] poly(N-vinylpyrrolidone)[2,6,11-13] and poly(ethylene glycol).[12,14] An anionic surfactant, sodium dodecylsulfate (SDS) was mainly used in these investigations. Neutral polymers and ionic surfactants form complexes of polyelectrolytic character, but interaction between them is weak and is believed to be mainly hydrophobic.

There are also reports on the studies on interaction between ionic polymers and ionic surfactants or hydrophobic ions of opposite charge.[5,15-22] The ionic polymers investigated include poly(styrenesulfonate)[5,15,17], poly(vinylsulfonate)[18], poly(methacrylate)[19] and polypeptides.[20-22] Luminescent probed methods[5,17,19] and potentiometry[15,16,18,20,21] using surfactant sensitive electrodes were main tools for the studies. Since polyelectrolytes interact strongly with oppositely charged surfactants due to coulombic force, drastic changes in properties of polymers upon binding with surfactants are expected. Moreover, synthetic polyelectrolytes are highly simplified analogues of biomacromolecules, and the binding study of the polyelectrolytes with surfactants is expected to give informations on the formation and physico-chemical properties of biomembranes.[23]

Poly(styrenesulfonate), PSS, contains both hydrophobic phenyl moiety and hydrophilic sulfonate group. This ionic polymer can interact with cationic surfactants by hydrophobic as well as electrostatic forces. This resembles the interaction of many biological macromolecules.

In this paper, we describe results of surface tensiometric investigation on the interaction of PSS with alkyltrimethylammonium salts. The effects of hydrocarbon chain length of the surfactants and salt on the interaction were examined. The results were also compared with those on poly(vinylsulfonate)/surfactant systems.

Experimental

Sodium salt of poly(styrenesulfonate), PSS, was purchased from Aldich and purified by reprecipitation from water by the addition of isopropyl alcohol. Molecular weight of PSS was determined from the intrinsic viscosity of the polymer in 0.05 M aqueous NaCl solution using the reported Mark-Houwink relationship,[24] $[\eta] = 1.39 \times 10^{-4} \times Mw^{0.72}$, of the polymer. Molecular weight of PSS was measured as 2.2 ×