second moment and other conditions. The original papers can be examined for details of the analyses.

The results for CH_3CH_2Cl are shown in Table II. The computed methyl group C–H bond lengths show a difference of 0.003 Å which is comparable to the 0.004 ± 0.004 Å in the reported r_z structure. For this compound, the infrared measurements of McKean[11] give a difference in the methyl group C–H bonds of 0.003 Å in the same direction. The agreement for relative bond lengths of these three very different methods is again satisfactory for the compound, but it will be seen below that the parallelism between the r_z and the r_e structures is not universal. Again, the absolute values of the corrected computed r_e C–H distances agree very well with the corrected experimental r_z values, and the overall agreement between the computed structure and the experimental microwave[13] and electron diffraction structures is satisfying.

The results for the two silicon compounds are given in Table III. For both of these substances, the asymmetry in the computed equilibrium methyl group C–H bond lengths is similar to that observed in the ethyl derivatives: a very small effect with the symmetric C–H longer than the asymmetric C–H by 0.002–0.003 Å. For CH_3SiH_2Cl,

the absolute r_e value of the asymmetric C–H bond agrees very well, as in the previous cases, with the corrected microwave r_z value. However, the symmetric C–H bond obtained from the experiment is excessively short in the r_s interpretation and correction for vibrational effects only makes it worse. The remainder of the computed structure of CH_3SiH_2Cl agrees well with the two microwave experimental results except for discrepancies in the angular distribution of the substituents on the silicon atom.

The computations reported here agree with the results of Zeil and Christen[1] in concluding that the substantial asymmetry of the methyl group in ethyl halides reported from microwave r_s measurements is an artifact of the substitution method of analysis and can be attributed to molecular vibrational effects. We show in addition, however, that a similar conclusion applies to the CH_3SiH_2X compounds. If the harmonic corrections of Zeil and Christen are based on an adequate force field, the asymmetry remaining in their r_z structures for the silicon compounds must result from anharmonic or internal rotation effects that are not accounted for in their analysis. Establishing the reality and approximate magnitude of the methyl group asymmetries is of importance in connection with the numerous attempts currently underway to provide a theoretical explanation of the intramolecular electronic interactions responsible for such asymmetry.

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Polarity at the Micelle–Water Interface under High Pressure As Estimated by a Pyrene-3-carboxaldehyde Fluorescence Probe

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The microscopic dielectric constants (ϵ) at micelle–water interfaces are estimated under high pressure (1–2610 bar) by use of pyrene-3-carboxaldehyde as fluorescence probe for environmental polarity. The microscopic values are evaluated as 48, 24, and 15 for sodium dodecyl sulfate (SDS), hexadecyltrimethylammonium chloride (HDTCl), and hexadecyltrimethylammonium bromide (HDTBr) at 1 bar. Additon of NaCl, and Na_2SO_4 to the SDS solution decreasess ϵ, whereas addition of ethanol causes ϵ to increase. The ϵ values rise with increasing pressure.

The microscopic polarity or the microscopic dielectric constant of the micellar interior and interface is a fundamental property of these microheterogeneous systems and a crucial characteristic for understanding micellar structure and function. Among available experimental methods for investigation of micropolarity, emission measurements using luminescence probes are particularly convenient.[2] Very recently, Thomas et al.[3] reported the application of pyrene-3-carboxaldehyde (PyCHO) for the evaluation of

the dielectric constant at the micelle–water interface. A linearity between the fluorescence maximum (λ_{max}) and the dielectric constant (ϵ, 10–80) of a series of protic ROH solvents was found. However, other solvent parameters in addition to the dielectric constant are probably important for the absolute value of ϵ.[4] In the present communication, the influence of high pressure on the dielectric constant of ionic detergents was studied with PyCHO as a fluorescence probe.

The influence of high pressure on the monomer fluorescence spectra of PyCHO in aqueous detergent solutions is displayed in Figure 1. The fluorescence intensity

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TABLE I: Estimates of the Dielectric Constants at Micelle–Water Interfaces under High Pressure at 25 °C

	ϵ					
system[a]	1[d]	450	990	1540	2070	2610
HDTBr	15, 37,[b] 16[c]	18	19			
HDTCl	24, 18[c]	24	26	30	30	29
SDS	48, 45[c]	51	52	53	54	54
SDS + NaCl (0.1 M)	46	49	49	51	53	52
SDS + NaCl (0.2 M)	45	49	51	51	51	52
SDS + NaCl (0.4 M)	44	46	47	49	49	
SDS + Na$_2$SO$_4$ (0.1 M)	45	45	50	51	53	
SDS + Na$_2$SO$_4$ (0.2 M)	45	49	50	49	52	
SDS + Na$_2$SO$_4$ (0.4 M)	43	44	46	45	49	
SDS + C$_2$H$_5$OH (0.1 M)	48	51	53	54	54	55
SDS + C$_2$H$_5$OH (0.3 M)	49	50	53	53	54	55
SDS + C$_2$H$_5$OH (1 M)	49	49	50	54	56	54
SDS + C$_2$H$_5$OH (2 M)	50	49	51	53	53	55

[a] [HDTBr] = [HDTCl] = [SDS] = 0.02 M.   [b] Shinitzky, M. *Isr. J. Chem.* **1974**, *12*, 879; at 24 °C.   [c] Reference 3.   [d] Pressure in bar.
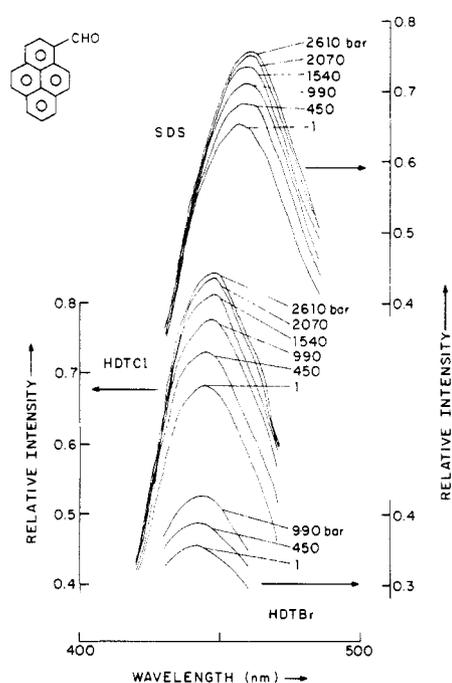

Figure 1. Fluorescence spectra of pyrene-3-carbonaldehyde in the presence of SDS, HDTCl, and HDTBr under high pressure. [SDS] = [HDTCl] = [HDTBr] = 0.02 M. Excited at 356 nm.

Figure 2. High-pressure influences on the dielectric constants of SDS (O), HDTCl (Δ), HDTBr (□), and ethanol (#) at 25 °C. Literature values for H$_2$O (X, 20 °C), C$_2$H$_5$OH (●, 30 °C), and n-C$_6$H$_{13}$OH (▲) are also given.

increases and the maximum (λ_{max}) shows a slight red shift with increasing pressure, i.e., λ_{max} shifts from 456.5, 444, and 439 nm for SDS, HDTCl, and HDTBr solutions at 1 bar to 459.5 (2610 bar), 446.5 (2610 bar), and 441 nm (990 bar), respectively. From Thomas' results,[3] it is concluded that the pressure increases the polarity or dielectric constant at micelle–water interface.

The dielectric constants (ϵ) experienced by the probe were estimated from the linear relationship between λ_{max} and ϵ obtained by Thomas et al., i.e., λ_{max} (nm) = 0.52ϵ + 431.5. The results are given in Table I and also shown graphically in Figure 2. We measured the λ_{max} values of PyCHO in absolute ethanol under high pressure and compared these results with the reference values for dielectric constants in order to check the reliability of the present experiments. The relative intensity of the fluorescence in ethanol increased by 58% by applying 2610 bar, and λ_{max} shifted from 443 nm (1 bar) to 448 nm (2610 bar). The dielectric constants of detergents examined increased with increasing pressure. The magnitudes of
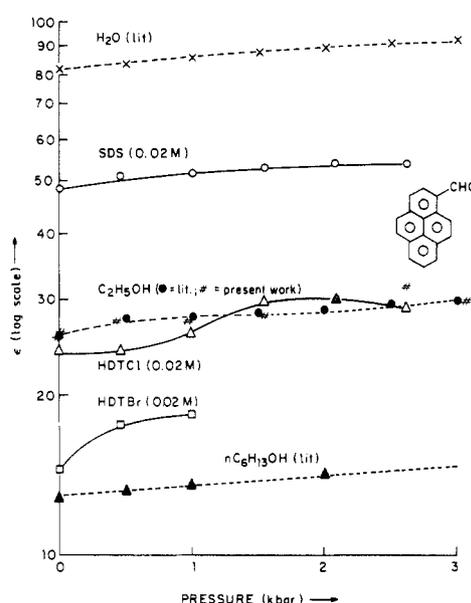
increase are between 13 and 50% and are in the order of HDTBr > HDTCl > SDS. On the other hand, the values of most solvents including water, aliphatic alcohols, and aliphatic hydrocarbons increase by only ca. 10% as the pressure is increased from 1 to 2000 bar.[8] Thus, it is concluded that the dielectric constant at the micelle–water interface increases more significantly than those of homogeneous solvents. The main reason for this effect is probably due to the increase in the dielectric constant of the water solvent, i.e., an increased interaction of water with the detergent's hydrocarbon chain with pressure. This enhanced water permeability might be due to the difference in the magnitudes of compressibilities of hydrocarbon cores and the interface regions.

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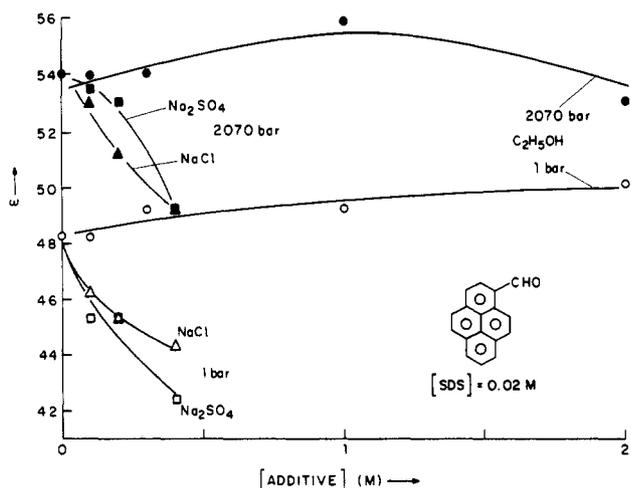
Figure 3. Influences of additives (C_2H_5OH, NaCl, and Na_2SO_4) and high pressure on the dielectric constants of SDS at 25 °C. [SDS] = 0.02 M; (O) C_2H_5OH, 1 bar; (△) NaCl, 1 bar; (□) Na_2SO_4, 1 bar; (●) C_2H_5OH, 2070 bar; (▲) NaCl, 2070 bar; (■) Na_2SO_4, 2070 bar.

As is seen in Table I and in Figure 3, ϵ's of SDS decreased with addition of NaCl and Na_2SO_4. This may be due to the penetration effect of the salts into the Stern layer and to the restriction in the mobility of the water molecules via electrostrictional hydration.[3,9,10] However, we should note here that the microviscosity near the interface of the hydrocarbon core decreases with addition of NaCl and Na_2SO_4.[11,12] This may mean that the Stern layer is less ordered in the presence of added salt.

On the other hand, addition of ethanol caused an increase in the microscopic dielectric constant. This may be due to the movement of ethanol molecules into the interface layer and to the disruptions of the Stern layer. This result also supports an increase in the mobility of water molecules into the micelle interior. In conclusion, although our results and conclusions are consistent with current models of micelle structure and dynamics, we are aware that interpretations of changes in an emission property as a function of a single parameter is a simplification and must be treated with proper caution. For example,[4] the protic character of a solvent or other specific interactions could lead to effects that amplify or cancel those due to the dielectric constant.

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Detection and Analysis of Anisotropic Tl²⁺ Centers in Glass

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A highly anisotropic Tl²⁺ center induced in soda silicate glasses by γ irradiation at 77 K has been detected by ESR. The parameters for the semioccupied molecular orbital were estimated through line-shape simulation of the hyperfine structure by using a newly developed solution to the spin Hamiltonian. Upon thermal annealing of the irradiated sample, the anisotropic Tl²⁺ center relaxed into a nearly isotropic one. This reflects a change in coordination of Tl²⁺ from axially distorted to spherical symmetry.

Introduction

p-block elements in the periodic table such as Tl^+, Pb^{2+}, and Sn^{2+} are important constituents of commercial glasses. In particular, Tl^+ has been utilized for manufacturing the gradient-index type optical waveguide[1] because of its large polarizability[2] compared with that of the other monovalent cations. However, detailed information on the coordination state of Tl^+ in glass has never been obtained.

We have succeeded in clarifying this problem by applying ESR; the thallous ion with the $6s^2$ electronic configuration is converted into paramagnetic Tl^{2+} ($6s^1$), trapping a hole upon γ irradiation. The geometry of the precursor is preserved in the product if the ESR measurements of the samples irradiated at 77 K are carried out at 77 K without an intervening warmup. Therefore, information on the chemical bonding state of Tl^+ can be obtained from detailed spin-Hamiltonian analysis and close line-shape fitting of the spectrum of Tl^{2+}.

Theory

There are two kinds of Tl nuclei, ²⁰³Tl (29.5%) and ²⁰⁵Tl (70.5%), and both have a nuclear spin $I = 1/2$.[3] Therefore, analysis of the hyperfine (hf) structure is made by assuming the following spin Hamiltonian:

$$\mathcal{H} = \beta S \cdot \tilde{g} \cdot H + I \cdot \tilde{A} \cdot S \qquad (1)$$

For X-band ESR measurement for Tl^{2+}, the magnitude of the latter term is considerably greater than that of the former.[4,10] When the $\tilde{g}$ and $\tilde{A}$ tensors can be approximated by scalars, that is, when the ligand field is practically spherically symmetric, the solution was given by Breit and Rabi.[5] However, the case in which the ligand field is heavily distorted, in general, does not have simple al-

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