Quantum mechanical calculations on molecular sieves. 1. Properties of the Si–O–T (T = Si, Al, B) bridge in zeolites

2 **AUTHORS**, INCLUDING:

Joseph G. Fripiat
University of Namur
107 PUBLICATIONS   **1,603** CITATIONS

effects of varying the concentration of water or solubilizate on the structure are manifest in a quantitative manner. The data should be useful for testing theoretical models of aggregation and phase behavior in amphiphile/water/solubilizate mixtures. More generally, the measurements should be useful in investigative applications of solubilizate–aggregate interactions. For example, combining such data with complementary NMR measurements on counterions, water, amphiphile, and solubilizate is expected to provide an insight into the molecular mechanism of the solubilization process and into the manner in which the solubilizate affects the mesophase stability. To demonstrate this strategy we have carried out a detailed study of solubilization in the bilayers of the lamellar phase of the potassium oleate/water system; the results will be published in the near future. A more detailed study

of the interaction of cholesterol with lecithin bilayers will also be published elsewhere.

Finally, we emphasize that the partial molecular surface area is just one example of a whole range of partial molecular properties that could be measured. We believe that measurements of these properties will provide a wealth of information about the relationship between molecular and interaggregate interactions and the structure and properties of lyotropic mesophases.

Quantum Mechanical Calculations on Molecular Sieves. 1. Properties of the Si–O–T (T = Si, Al, B) Bridge in Zeolites

E. G. Derouane*[†] and J. G. Fripiat[†]

Central Research Laboratories, Mobil Research and Development Corporation, Princeton, New Jersey 08540 (Received: June 4, 1986)

Ab initio (nonempirical) molecular orbital calculations have been performed to investigate the behavior and the stability of Si–O–T bridges such as found in zeolites. Dimeric model clusters of the type $(OH)_3Si–OM–T(OH)_3$, where M is a monovalent charge compensating cation and T is Si, Al, or B, were considered. It is shown that elongation of the T–O bond, upon replacement of Si by Al, occurs preferentially by a local deformation of the Si–O–Al bridges, i.e., a rearrangement of the O atoms directly coordinated to Al. The stability of the Si–O–T bridge increases with the electropositive character of the charge compensating cation M. The H form of the boron-containing cluster appears particularly unstable, suggesting that tetrahedrally coordinated framework boron in the hydrogen form of crystalline borosilicates has poor stability.

Introduction

Quantum chemical ab initio calculations may be a help to investigate the stability and the behavior of Si–O–T bridges (T = Si, Al, or B) in zeolite frameworks, in particular because such properties are not always easily quantitated by experimental means.[1] Quantum chemical calculations become reasonable when the cluster model is adopted. However, for computational reasons, the size of the clusters is determined by the choice of the theoretical method. The restricted Hartree–Fock–Roothaan (LCAO-SCF-MO) approach has proved to be successful in zeolite and silica chemistry as shown, for example, by the works of Sauer et al.,[2–4] Hass et al.,[5,6] Geisinger et al.,[7] Mortier et al.,[8] and Derouane et al.[9–12] Generally, in these studies,[1–8] idealized geometries were used for the model clusters. In contrast, the models chosen in our previous investigations[9–12] reflected more intimately the structure of the zeolites under study as they were derived from crystallographic structural data. The latter remark holds also for the geometry of the bridge clusters considered in the present investigation.

This paper examines the effect of various cations, i.e., H^+, Li^+, and Na^+, on the charge distribution and stability of the Si–O–Al and Si–O–B bridges in zeolites, and discusses possible mechanisms by which the T–O bond can be elongated by relaxation of the framework upon substitution of Si by Al.

Theoretical Method and Models

Restricted Hartree–Fock–Roothaan results were obtained by using the STO-3G basis set[13,14] and the GAUSSIAN-80 program

TABLE I: Interatomic Distances[24]

bond	distance, nm	bond	distance, nm
O–H	0.0975	B–O(1)	0.136
Si–O	0.160	H–O(1)	0.0975
T–O	0.160	Li–O(1)	0.200
S–O(1)	0.160	Na–O(1)	0.229
Al–O(1)	0.176		

package,[15] adapted for the 36-bit computerword of the Digital DEC 20/60 computer. All bielectronic integrals larger than 10^{-6}

(1) Sauer, J.; Zahradnik, R. *Int. J. Quantum Chem.* **1984**, *26*, 793.
(2) Sauer, J.; Hozba, P.; Zahradnik, R. *J. Phys. Chem.* **1980**, *84*, 3318.
(3) Sauer, J.; Engelhardt, G. *Z. Naturforsch.* **1982**, *37a*, 277.
(4) Sauer, J. *Acta Phys. Chem.* **1985**, *31*, 19.
(5) Hass, E. C.; Mezey, P. G.; Plath, P. J. *J. Mol. Struct.: THEOCHEM* **1981**, *76*, 389.
(6) Hass, E. C.; Mezey, P. G.; Plath, P. J. *J. Mol. Struct.: THEOCHEM* **1982**, *87*, 261.
(7) Geisinger, K. L.; Gibbs, G. V.; Natrotsky, A. *Phys. Chem. Miner.* **1985**, *11*, 266.
(8) Mortier, W. J.; Sauer, J.; Lercher, J. A.; Noller, H. *J. Phys. Chem.*, **1984**, *88*, 905.
(9) Fripiat, J. G.; Berger-André, F.; André, J. M.; Derouane E. G. *Zeolites* **1983**, *3*, 306.
(10) Derouane, E. G.; Fripiat, J. G. In Proceedings of the 6th International Zeolite Conference; Olson, D. H., Bisio, A., Eds.; Butterworths: Guildford, UK, 1984; p 717.
(11) Derouane, E. G.; Fripiat, J. G. *Zeolites* **1985**, *5*, 165.
(12) Fripiat, J. G.; Galet, P.; Delhalle, J.; André, J. M.; Nagy, J. B.; Derouane, E. G. *J. Phys. Chem.* **1985**, *89*, 1932.
(13) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.
(14) Hehre, W. J.; Ditchfield R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, *64*, 5142.

[†] Present address: Center for Advanced Material Research, Facultés Universitaires Notre-Dame de la Paix, 61, rue de Bruxelles, B-5000 Namur, Belgium.
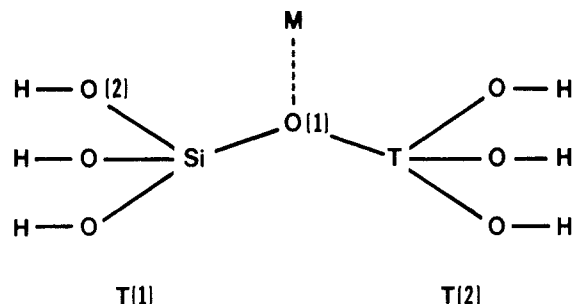
Figure 1. Dimeric model cluster (T is Si, Al, or B and M is H, Li, or Na).

were explicitly taken into account and the convergence threshold on the density matrices was less than 5×10^{-5}.

The model cluster shown in Figure 1 was considered. Ideal tetrahedral environments around Si, Al, or B were assumed with H-O-Si, H-O-Al, H-O-B, O-Si-O, O-Al-O, and O-B-O angles equal to 109.471°. The charge compensating cation, M, was located above O(1) in the Si-O(1)-T plane, the Si-O(1)-T angle being of 144°. The interatomic distances used in the calculations are listed in Table I. The selected Si-O, Al-O, and B-O bond lengths are calculated by using the ionic radii of elements.[24]

In the calculations on dimers with a metal cation, using small atomic orbital basis sets (such as STO-3G), an additional and unwanted stabilization energy term may appear. It results essentially from the different extensions of the atomic orbitals basis set for the subsystems (dimers without cation) and the supersystems (dimers with cation). This factor must be accounted for when comparing these two systems.[2] The Boys-Bernardi counterpoise method (BSSE)[16-18] takes into account this type of error. In our particular case, it involves the calculation of the dimer anion energy using the full set of expansion functions for the supersystem (neutral dimer).

Results and Discussion

1. Framework Relaxation upon Substitution of Si by Al. First, we discuss below the structural relaxation of the Si-O-T bridge, as it should occur upon substitution of T (Si by Al), when the M cation is a proton. Three types of T-O bond elongation process have been considered as possible models for the framework relaxation.

A first process consists in a progressive *stretching* (I) of the Al-O(1) bond, the whole T(2) unit translating away from O(1) along the T-O(1) direction. No angles are altered by this motion. A second possibility to increase the Al-O bond length is a *rotation* (II) of the whole T(1) unit around an axis going through Si and perpendicular to the Si-O(1)-Al plane. This process alters the value of the Al-Si-O(1) and Al-O(1)-Si angles. Finally, one can also consider the *deformation* (III) of the Si-O-Al bridge in which only the bridging O(1) atom (with H) moves away from Al although maintaining the same Si-O(1) bond length. In the latter case, both the Al-Si-O(1) and O(1)-Si-O(2) angles are changed.

Table II lists relative relaxation energies and the charges on O(1) and H (located at position M) for the three above-mentioned relaxation processes, the various configurations being characterized by the Al-O(1) bond length and the Al-Si-O(1) and O(1)-Si-O(2) angles. Relative relaxation energies are plotted as a function of the Al-O(1) bond length in Figure 2. The dimer with Si-O and Al-O bond lengths equal to 0.160 nm is taken as energy reference.

When relaxation occurs by stretching (I) of the Al-O(1) bond, a minimum is found near 0.183 nm. The latter value compares

(15) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; Defrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE*, **1981**, *13*, 406, adapted by J. G. Fripiat, Facultés Universitaires de Namur, Belgium.
(16) Boys, S. F.; Bernardi, F. *J. Mol. Phys.* **1970**, *30*, 553.
(17) Johanssen, A.; Kollman, P.; Rothenberg, S. *Theor. Chim. Acta*, **1973**, *29*, 167.
(18) Urban, M.; Hobza, P. *Theor. Chim. Acta* **1975**, *36*, 207.

TABLE II: Relaxation of the Si-O-Al Bridge in Model Dimers

Al-O(1) length, nm	Al-Si-O(1) angle, deg	O(1)-Si-O(2) angle, deg	rel energy, kcal/mol	charge O(1)	charge H
		I. Stretching			
0.160	35.264	109.471	0.0	-0.571	0.313
0.164	35.264	109.471	-6.3	-0.563	0.310
0.168	35.264	109.471	-10.8	-0.556	0.307
0.172	35.264	109.471	-14.0	-0.550	0.304
0.176	35.264	109.471	-16.0	-0.546	0.301
0.180	35.264	109.471	-16.9	-0.543	0.298
0.184	35.264	109.471	-17.1	-0.540	0.294
0.188	35.264	109.471	-16.6	-0.538	0.291
0.192	35.264	109.471	-15.5	-0.537	0.288
		II. Rotation			
0.160	35.264	109.471	0.0	-0.571	0.313
0.167	37.736	109.471	-5.1	-0.558	0.309
0.173	40.207	109.471	-6.1	-0.549	0.306
0.180	42.679	109.471	-3.8	-0.544	0.302
		III. Deformation			
0.160	35.264	109.471	0.0	-0.571	0.313
0.167	37.736	107.000	-5.8	-0.559	0.311
0.173	40.207	104.528	-7.1	-0.552	0.309
0.180	42.679	102.057	-4.8	-0.547	0.307

TABLE III: Heterolytic Dissociation Energies in Al and B Dimers (in kcal/mol)

bond	(Si,Al)	(Si,B)
H-O(1)	392	370
Li-O(1)	164	169
Na-O(1)	120	127

TABLE IV: Relative Heats of Formation of Al and B Dimers[a]

dimer	E_F, kcal/mol	dimer	E_F, kcal/mol
Al,Na	-94.0	B,Na	47.8
Al,Li	6.0	B,H	173.8
Al,H	0.0		

[a] Referred to the Na form of the aluminosilicate dimer.

well with the sum of the ionic radii of Al^{3+} and O^{2-} (0.183 nm). This situation corresponds to an idealized relaxation of the Al-O bond which cannot take place in a rigid zeolite framework. It indicates however that the highest energy stabilization gained by elongating the T-O bond when Al replaces Si (with H^+ as a counterion) is equal to 17.1 kcal/mol per bond.

When relaxation occurs by rotation (II) of the T(1) unit or by deformation (III) of the Si-O-Al bridge, energy minima are found at ca. 0.172 and 0.174 nm, respectively. The latter values are close to the experimental Al-O bond length (0.176 nm) observed in crystalline aluminosilicates. Relaxation by rotation (II), which involves all the oxygen atoms surrounding Si, is found to be slightly less favorable than relaxation by deformation (III) of the Si-O(1)-Al bridge. The latter affects only the oxygen atoms in the immediate coordination sphere of Al and appears as the most probable restructuring process when Al substitutes Si.

In these three cases, the formal negative charge (ca. -0.55) on oxygen decreases uniformly as the Al-O bond length increases whereas a much smaller variation is observed for the formal positive charge (ca. 0.3) on hydrogen. It is interesting to note that relaxation by deformation (III) is the process which maintains the highest ionic character to the O(1)-H bond when the dimers obtained from I, II, or III are compared at their energy minimum. It suggests that process III could also favor the achievement of higher protonic acid strengths.

2. Contribution of Various Cations to the Stabilization of the Si-O-Al Bridge. The second part of this discussion deals with the relative effects of various cations, i.e., H^+, Li^+, and Na^+, on the charge distribution and the stability of the Si-O-Al bridge. Heterolytic dissociations energies, taking into account the BSSE corrections, were evaluated for the M-O(1) bonds. The dimeric clusters stabilities are compared, as well as the changes in their atomic charges, when the nature of the cation is varied.

TABLE V: Distribution of Atomic Charges in Al and B Dimers

site	Na as counterion		Li as counterion		H as counterion	
	(Si,Al)	(Si,B)	(Si,Al)	(Si,B)	(Si,Al)	(Si,B)
OH(Si)[a]	−0.384	−0.371	−0.348	−0.339	−0.333	−0.324
Si	1.379	1.440	1.440	1.485	1.487	1.521
O(1)	−0.722	−0.614	−0.582	−0.514	−0.533	−0.459
M[b]	0.858	0.871	0.382	0.410	0.276	0.329
T[c]	1.227	0.483	1.280	0.520	1.271	0.496
OH(T)[a]	−0.530	−0.356	−0.492	−0.294	−0.501	−0.305

[a] Terminal hydroxyl groups bound respectively to Si and T (Al or B).   [b] Na, Li, or H as counterions.   [c] Al or B.
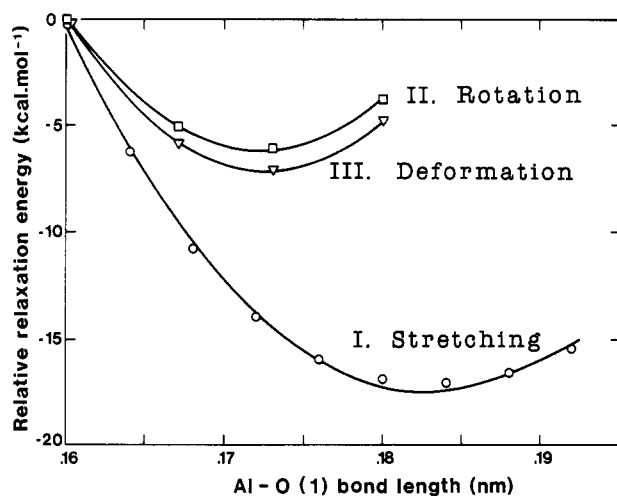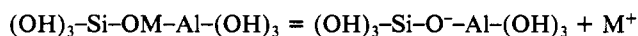

Figure 2. Relative relaxation energy in the Si–O–Al model dimers.

2.1. Heterolytic Dissociation Energies of the M–O(1) Bonds. Heterolytic dissociation energies are readily evaluated by considering hypothetical reactions of the type

$$(OH)_3-Si-OM-Al-(OH)_3 = (OH)_3-Si-O^- -Al-(OH)_3 + M^+$$

for which all terms can be computed.

The values of Table III hold for the complete and heterolytic rupture of the M–O(1) bond and for nonhydrated M cations. As expected, they decrease as the M–O(1) bond becomes more ionic (see the M and O(1) formal charges in Table V).

2.2. Relative Stability of the Si–O–Al Bridges. The relative stabilities of the Si–O–Al bridge associated with different M cations can be compared by computing the heat of formation of the corresponding dimeric clusters, i.e., the quantity

E(formation) =
cluster's total energy − sum of the individual atom energies

and by arbitrarily taking as reference the heat of formation of the protonated Si–O–Al bridge. The calculated values are listed in Table IV. They suggest that the Si–O–Al bridge becomes less stable when Na is exchanged by H or Li. Per exchange site, the protonated form appears about 94 kcal/mol less stable than the Na form.

The above results refer of course to systems in which the cations are not hydrated. Hydration is expected to reduce the difference between these three cases and to bring the Li system more in line with the Na system. Nevertheless, it can reasonably be proposed that the reduced stability of the protonated bridge contributes to the observed lower thermal stability of the hydrogen form of zeolites, in particular when they have a high Al content.

2.3. Electronic Populations vs. Cation Nature. Varying the cation appears to alter dramatically the distribution and magnitude of the atomic charges. Table V lists those for all three cases.

It is seen that the M–O bond becomes progressively more ionic when the proton is replaced by more electropositive cations. As their electropositive character increases (H < Li < Na), the excess negative charge, originally largely delocalized in the cluster, gets progressively more localized on the O(1) oxygen as a mirror charge for the positive M cation. Consequently, the positive charges on Si and Al bound to O(1) are also reduced, the effect being more

pronounced for Si which is more electronegative than Al.

The broad delocalization of the negative charge in the clusters supports the idea that zeolite frameworks have a highly covalent nature (as obvious also from the low formal charges on Si and Al). The anionic framework must hence be considered to behave as a soft base, a view which may help rationalizing several zeolite properties such as their ion-exchange selectivity, their high affinity for bulky polarizable (organic) cations (soft acids), etc.[10,11]

2.4. Relative Stabilities of the Al- and B-Containing Dimers. Table IV lists the relative heats of formation of Al- and B-containing dimers, calculated as described above, in the presence of H and Na counterions, respectively. For both the aluminosilicate and borosilicate dimers, the H form is at least about 100 kcal/mol less stable that the Na form. Replacement of Al by B destabilizes the cluster by about 150 kcal/mol. The conjunction of both effects leads to a highly unstable protonated borosilicate dimer. This observation suggests that tetrahedral boron has poor stability in the framework of protonated boro(alumino)silicates, which agrees with other theoretical calculations.[19]

Additional information is gained by considering the atomic charges distributions (see Table V). The atomic centers are defined in the model. A similar charge distribution pattern is observed in all cases. As expected, the M–O(1) bond becomes more ionic when H is replaced by more electropositive species such as Li and Na. The formal positive charge on B is only about 40% of that of Al, in agreement with its higher electronegativity. As shown by the difference between the positive and negative charges, the M–O(1) bond is the B-containing clusters is, in all cases, less polar (ionic) than in the Al-containing clusters. These conclusions are consistent with the weak protonic acidity of Brønsted sites in crystalline borosilicates.[20–23]

Conclusions

The following conclusions are proposed:

1. Upon substitution of Si by Al at a given structural T site, relaxation occurs preferentially by a local deformation of the Si–O–Al bridges, i.e., by a rearrangement of the oxygen atoms directly coordinated to Al.

2. This relaxation scheme which allows for the rigidity of the rest of the framework is also the deformation which maximizes the ionicity of the bridging hydroxyl group. This effect could explain partially the difference in acid strength of Brønsted sites in crystalline and amorphous aluminosilicates.

3. The stability of Si–O–Al bridges is affected by the nature of the charge compensating cation. Higher stability is observed for more electropositive countercations. In addition the hydrogen form of a dehydrated zeolite appears intrinsically less stable than its sodium counterpart. This effect should obviously become more

(19) Pelmentschikov, A. G.; Zhidomirov, G. M.; Khuroshvili, D. V.; Tsitsishvili, G. V. In *Structure and Reactivity of Modified Zeolites*; Jacobs, P. A., et al., Eds.; Elsevier Science: Amsterdam, 1984, p 85.

(20) Derouane, E. G.; Baltusis, L.; Dessau, R. M.; Schmitt, K. D. *Stud. Surf. Sci. Catal.* **1985**, *20*, 135.

(21) Scholle, K. F. M. G. J.; Kentgens, A. P. M.; Veeman, W. S.; Frenken, P.; Van der Velden, G. P. M. *J. Phys. Chem.* **1984**, *88*, 5.

(22) Chang, C. D.; Chu, C. T. W.; Kuehl, G. H.; Lago, R.M. *Prepr.—Div. Pet. Chem., Am. Chem. Soc.* **1985**, *30*(1), 195.

(23) Chu, C. T. W.; Chang, C. D. *J. Phys. Chem.* **1985**, *89*, 1569.

(24) Huhey, J. E.; *Inorganic Chemistry, Principles of Structure and Reactivity*; Harper: New York, 1978; p 71.

apparent as Al content increases.

4. Boron-containing dimers are less stable than their Al-containing analogues. The H form of the boron dimer is the most unstable species. Its hydroxyl group appears less polar than the corresponding one in the Al dimer. These observations support the finding that Brønsted sites in crystalline borosilicates are weak compared to those of their Al analogues. They suggest in addition that tetrahedrally coordinated boron in the hydrogen form of

framework borosilicates is unlikely to be highly stable.

Variation in Nitroxide Probe Chain Flexibility within Sodium Dodecyl Sulfate Hemimicelles

Prem Chandar,[†] **P. Somasundaran,**[*†] **Kenneth C. Waterman,**[‡1] **and Nicholas J. Turro**[*‡]

School of Engineering and Applied Science, and Department of Chemistry, Columbia University, New York, New York 10027 (Received: June 30, 1986; In Final Form: September 2, 1986)

Three nitroxide spin probes (5-, 12-, and 16-doxylstearic acid) were used to investigate the structure of sodium dodecyl sulfate (SDS) micelles and the interfacial layer between water and alumina formed by SDS (hemimicelles of SDS). It was found that whereas the rotational correlation times of the three probes differ in SDS micelles, the effective microviscosities of the probes are the same. In contrast, the microviscosity within the SDS hemimicelles varies according to the distance from the alumina surface: the nitroxide sees a more ordered environment as it is placed closer to the alumina. This represents the first report of variations in flexibility (microviscosity) within a hemimicelle.

The science of the water–solid interfacial layer formed by adsorbed long-chain surfactants on solids has been studied extensively for its value in the fields of enhanced oil recovery,[2] flotation,[3] detergency,[4] lubrication,[5] and microelectronics.[6] Considerable experimental evidence is consistent with the postulate that such surfactants form localized aggregates (termed hemimicelles) on the solid surface.[7] The evidence for hemimicelles has generally been indirect, and hemimicelle structure and dynamics have been inferred from measurements of bulk properties using such techniques as adsorption isotherms, ζ potentials, particle wettability, and heats of adsorption.[8] Recently we reported the use of two types of molecular probes for use in spectroscopic investigations of the hemimicelle microstructure formed by sodium dodecyl sulfate (SDS) adsorbed on alumina. The first involved studies of pyrene and dinaphthylpropane fluorescence,[9] while the second involved the spin probe 16-doxylstearic acid (**1**), a stable nitroxide radical, for use with ESR spectroscopy.[10] The carboxylate functionality of this latter probe adsorbs on the positively charged alumina surface. Our results indicated that at pH 6.5 this probe aggregates mostly by itself on the surface at low SDS concentrations and forms cohemimicelles with the SDS at higher SDS concentrations. The relative anisotropy observed in an ESR spectrum is directly related to the rotational mobility of the probe, a term that can be correlated with the probe's microviscosity.[11] Using this correlation, we were able to deduce that the environment within the SDS hemimicelle is relatively viscous. In both these studies of the microenvironment of the SDS hemimicelle, the data reported represent a single probe position within the hemimicelle (or a time average of many depths from the surface).

Spin probes have been used extensively to study the microviscosity and micropolarity of membranes, multilayers, and micelles.[12] In particular, doxylstearic acid spin probes have been useful in determining these parameters for different probe depths within phospholipid bilayers and micelles. Such studies have provided information on the orientation of the probes within the systems as well as information on the microenvironmental differences within the bilayer or micelle. In this communication, we wish to report the use of three doxylstearic acid derivatives, 16-, 12-, and 5-doxylstearic acids (**1**, **2**, and **3**, respectively) in

the ESR investigation of SDS micelles in water and SDS hemimicelles at the water–alumina interface. The results reported here should be viewed as preliminary, bearing in mind the usual

(1) NIH Postdoctoral fellow.

(2) (a) Hanna, H. S.; Somasundaran, P. In *Improved Oil Recovery by Surfactant and Polymer Flooding*; Shah, D. O., Schecter, R. S., Eds.; Academic: New York, 1977. (b) Somasundaran, P.; Chandar, P. In *Solid–Liquid Interactions in Porous Media*; Technip: Paris, 1985; pp 411–428.

(3) (a) Aplan, F. F.; Fuerstenau, D. W., In *Froth Flotation*; Fuerstenau, D. W., Ed.; AIME: New York, 1962. (b) Somasundaran, P. *AIChe. Symp. Ser.* **1975**, *71*(150), 1–15.

(4) Schwuger, M. J. *Surfactant Sci. Ser.* **1981**, *11*.

(5) Shilling, G. J.; Bright, G. S. *Lubrication* **1977** *63*(2), 13–24.

(6) Mittal, K. L., Ed. *Solution Chemistry of Surfactants*; Plenum: Press: New York, 1979; Vol. 1, 2.

(7) Gaudin, A. M.; Fuerstenau, D. W. *Trans. AIME* **1955**, *202*, 66–72.

(8) (a) Somasundaran, P.; Healy, T. W.; Fuerstenau, D. W. *J. Phys. Chem.* **1964**, *68*, 3562. (b) Hough, D. B.; Rendall, H. M. In *Adsorption from Solution at the Solid–Liquid Interface*; Parfitt, G. D., Rochester, C. H., Eds.; Academic: New York, 1983. (c) Fuerstenau, D. W. *Trans. AIME* **1957**, 1365–1367. (d) Somasundaran, P.; Chandar, P.; Chari, K. *Colloids Surf.* **1983**, *8*(2).

(9) (a) Chandar, P.; Somasundaran, P.; Turro, N. J. *J. Colloid Interface Sci.*, in press. (b) Somasundaran, P.; Turro, N. J.; Chandar, P. *Colloids Surf.*, in press. (c) Levitz, P.; van Damme, H.; Keravis, D. *J. Phys. Chem.* **1984**, *88*, 2228–2235.

(10) Waterman, K. C.; Turro, N. J.; Chandra, P.; Somasundaran, P. *J. Phys. Chem.*, in press.

(11) See, for example: (a) Libertini, L. J.; Waggoner, A. S.; Jost, P. C.; Griffith, O. H. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *64*, 13–19. (b) Ohnishi, S.; Cyr, T. J. R.; Fukushima, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 673–676. (c) Oakes, J. *Nature (London)* **1971**, *231*, 38–39. Baglioni, P.; Ottaviani, M. F.; Martini, G.; Ferroni, E. In *Surfactants in Solution*; Mittal, K. L., Lindamm, B., Eds.; Plenum: New York, 1984; Vol. 11, pp 541–557. (d) Sackman, E.; Trauble, H. *J. Am. Chem. Soc.* **1972**, *94*, 4482–4491, 4492–4498, 4499–4510. (e) Jost, P. C.; Griffith, O. H.; Capaldi, R. A.; Vanderkooi, G. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 480–484. (f) Schindler, H.; Seelig, J. *J. Chem. Phys.* **1974**, *61*, 2946–2949. (g) Yamaguchi, T.; Yamauchi, A.; Kimoto, E.; Kimizuka, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 372–376. (h) Aizawa, M.; Komatsu, T.; Nakagawa, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 975–979. (i) Isshiki, S.; Uzu, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3205–3206. (j) Ottaviani, M. F.; Baglioni, P.; Martini, G. *J. Phys. Chem.* **1983**, *87*, 3146–3153. (k) Robinson, B. H.; Beth, A. H. *Electron Spin Reson.* **1983**, *8*, 346–377. (l) Lai, C.-S. *Electron Spin Reson.* **1985**, *7*, 246–290; **1986**, *10A*, 116–146.

(12) (a) Hubbell, W. L.; McConnell, H. M. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *64*, 20–27. (b) Smith, I. C. P. *Chimia* **1971**, *25*, 349–360. (c) Yoshioka, H. *J. Am. Chem. Soc.* **1979**, *101*, 28–32. (d) Libertini, L. J.; Waggoner, A. S.; Jost, P. C.; Griffith, O. H. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *64*, 13–19. (e) Jost, P. C.; Griffith, O. H.; Capaldi, R. A.; Vanderkooi, G. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 480–484.

†School of Engineering and Applied Science.
‡Department of Chemistry.