Zwitterionic (Ammoniomethyl)tetrafluorosilicates of the Formula Types $F_4SiCH_2NH_2(CH_2)_nMe$ ($n = 5-11$) and $F_4SiCH_2NMe_2(CH_2)_5Me$: A New Class of Highly Efficient Surface-Active Compounds

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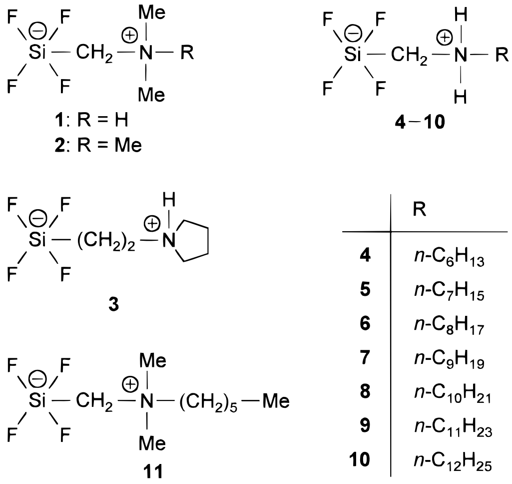
The zwitterionic (ammoniomethyl)tetrafluorosilicates $F_4SiCH_2NH_2(CH_2)_nMe$ ($n = 5-11$; compounds **4**−**10**) were synthesized by reaction of the corresponding (aminomethyl)triethoxysilanes $(EtO)_3SiCH_2NH(CH_2)_nMe$ ($n = 5-11$; compounds **13**−**19**) with HF. The silanes **13**−**19** were obtained by reaction of $(EtO)_3SiCH_2Cl$ with the corresponding *n*-alkylamines $H_2N(CH_2)_nMe$ ($n = 5-11$). The zwitterionic (ammoniomethyl)tetrafluorosilicate $F_4SiCH_2NMe_2(CH_2)_5Me$ (**11**), the *N*,*N*-dimethyl derivative of **4**, was synthesized by reaction of $(MeO)_3SiCH_2NMe_2$ with n-$C_6H_{13}Br$, followed by reaction of the resulting quaternary ammonium salt $[(MeO)_3SiCH_2NMe_2(CH_2)_5Me]Br$ with HF. Compounds **4**−**11** are characterized by the presence of a pentacoordinate (formally negatively charged) silicon atom and a tetracoordinate (formally positively charged) nitrogen atom. $F_4SiCH_2NH_2(CH_2)_9Me$ (**8**) was structurally characterized by single-crystal X-ray diffraction. The coordination polyhedron around the silicon atom of **8** in the crystal is a slightly distorted trigonal bipyramid, with fluorine atoms in the axial positions (Berry distortion 8%). Intermolecular N−H···F hydrogen bonds influence the packing of the zwitterions in the crystal. Surface tension measurements with solutions of **4**−**11** in 0.01 M hydrochloric acid demonstrated that these compounds are highly efficient surfactants. Increase of the *n*-alkyl chain length (**4** → **10**) was found to result in an increase of surface activity. The equilibrium surface tension vs concentration isotherms for **4** and **11** (solutions of "surface-chemically pure" samples in 0.01 M hydrochloric acid) were analyzed quantitatively and the surface thermodynamics of these surfactants interpreted on the molecular level. Preliminary studies demonstrated that aqueous solutions of **4**−**11** led to a hydrophobizing of glass surfaces.

Introduction

In a series of recent papers, we have reported on the synthesis and structural characterization of some zwitterionic (ammonioorganyl)tetrafluorosilicates, such as compounds **1**−**3** (see Chart 1).[1] These molecular λ^5*Si*-silicates are characterized by the presence of a pentacoordinate (formally negatively charged) silicon atom and a tetracoordinate (formally positively charged) nitrogen atom. Here we report on the synthesis of a series of related (ammoniomethyl)tetrafluorosilicates of the formula type $F_4SiCH_2NH_2(CH_2)_nMe$ ($n = 5-11$; compounds **4**−**10**) and their physical characterization as surfactants. The *N*,*N*-dimethyl derivative of **4** (compound **11**) was included in these studies. In addition, the crystal structure of compound **8** is reported. As the λ^5*Si*-silicates **4**−**11** contain a polar (zwitterionic) hydro-

Chart 1



	R
4	*n*-C_6H_{13}
5	*n*-C_7H_{15}
6	*n*-C_8H_{17}
7	*n*-C_9H_{19}
8	*n*-$C_{10}H_{21}$
9	*n*-$C_{11}H_{23}$
10	*n*-$C_{12}H_{25}$

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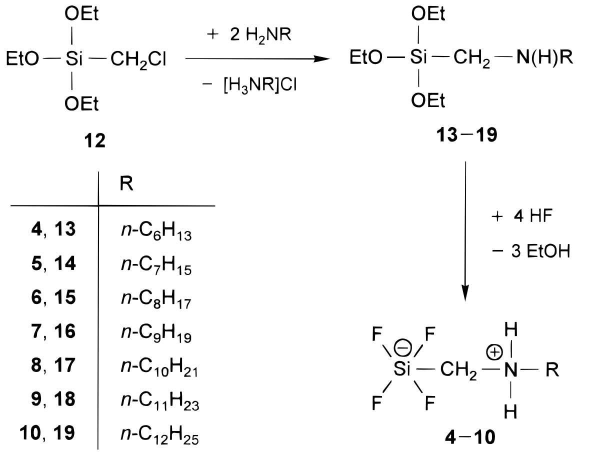
(1) Publications on zwitterionic λ^5*Si*-fluorosilicates: (a) Tacke, R.; Becht, J.; Mattern, G.; Kuhs, W. F. *Chem. Ber.* **1992**, *125*, 2015−2018. (b) Tacke, R.; Lopez-Mras, A.; Becht, J.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1012−1016. (c) Tacke, R.; Becht, J.; Lopez-Mras, A.; Sheldrick, W. S.; Sebald, A. *Inorg. Chem.* **1993**, *32*, 2761−2766. (d) Tacke, R.; Becht, J.; Dannappel, O.; Ahlrichs, R.; Schneider, U.; Sheldrick, W. S.; Hahn, J.; Kiesgen, F. *Organometallics* **1996**, *15*, 2060−2077.

S0276-7333(98)00021-1 CCC: $15.00

Scheme 1



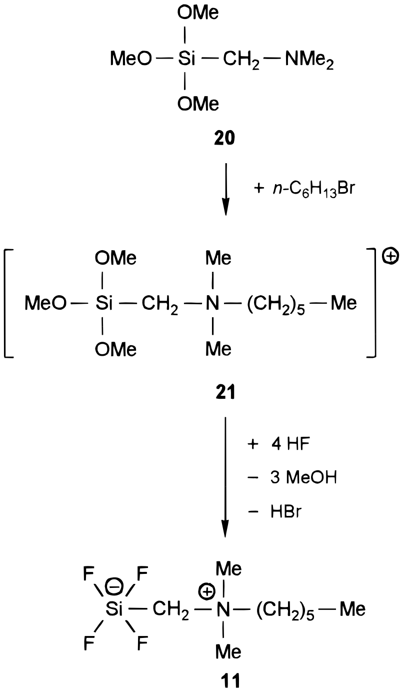
	R
4, **13**	n-C_6H_{13}
5, **14**	n-C_7H_{15}
6, **15**	n-C_8H_{17}
7, **16**	n-C_9H_{19}
8, **17**	n-$C_{10}H_{21}$
9, **18**	n-$C_{11}H_{23}$
10, **19**	n-$C_{12}H_{25}$

philic moiety and a long lipophilic alkyl group, they were expected to exhibit surface-active properties. The studies presented here were carried out as a part of our systematic studies[1,2] on zwitterionic (molecular) λ^5*Si*-silicates (for reviews and proceedings on pentacoordinate silicon compounds, see ref 3).

Results and Discussion

Syntheses. The zwitterionic (ammoniomethyl)tetrafluorosilicates **4−10** were prepared by two-step syntheses, starting from (chloromethyl)triethoxysilane (**12**) (Scheme 1). In the first step, the (aminomethyl)triethoxysilanes **13−19** were synthesized by reaction of **12** with the corresponding *n*-alkylamine $H_2N(CH_2)_nMe$ ($n = 5-11$) in boiling toluene. Compounds **13−19** were isolated in 53−65% yield as colorless liquids. Subsequent reaction of **13−19** with hydrogen fluoride in a mixture of 48% hydrofluoric acid and ethanol at 0 °C yielded the title compounds **4−10**. Upon recrystallization from ethanol, **4−10** were isolated in 73−92% yield as colorless, crystalline solids.

Scheme 2



The zwitterionic (ammoniomethyl)tetrafluorosilicate **11** was synthesized by a two-step synthesis, starting from [(dimethylamino)methyl]trimethoxysilane (**20**) (Scheme 2). In the first step, the quaternary ammonium bromide **21** (crude product; not characterized) was prepared by reaction of **20** with *n*-hexyl bromide in boiling acetonitrile. Subsequent reaction of **21** with hydrogen fluoride yielded the title compound **11**. The reaction **21** → **11** was again carried out in a mixture of 48% hydrofluoric acid and ethanol at 0 °C. Upon recrystallization from ethanol, compound **11** was isolated in 86% yield (related to **20**) as a colorless, crystalline solid.

The identities of **4−11** and **13−19** were established by elemental analyses (**4−11**, C, H, F, N; **13−19**, C, H, N), multinuclear solution-state NMR studies (**4−11**, ^1H, ^{13}C, ^{19}F; **13−19**, ^1H, ^{13}C, ^{29}Si),[4] and mass-spectrometric investigations (**4−11**, FAB MS; **13−19**, EI MS). In addition, compound **8** was characterized by a crystal structure analysis.

Crystal Structure Analysis of 8. The crystal structure of the zwitterionic λ^5*Si*-silicate **8** was determined by a single-crystal X-ray diffraction study. The crystal data and experimental parameters used for this analysis are given in Table 1 (for further details, see the Experimental Section). The molecular structure of

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(2) Publications on zwitterionic spirocyclic λ^5*Si*-silicates: (a) Strohmann, C.; Tacke, R.; Mattern, G.; Kuhs, W. F. *J. Organomet. Chem.* **1991**, *403*, 63−71. (b) Tacke, R.; Sperlich, J.; Strohmann, C.; Mattern, G. *Chem. Ber.* **1991**, *124*, 1491−1496. (c) Tacke, R.; Sperlich, J.; Strohmann, C.; Frank, B.; Mattern, G. *Z. Kristallogr.* **1992**, *199*, 91−98. (d) Tacke, R.; Wiesenberger, F.; Lopez-Mras, A.; Sperlich, J.; Mattern, G. *Z. Naturforsch. B* **1992**, *47*, 1370−1376. (e) Tacke, R.; Lopez-Mras, A.; Sheldrick, W. S.; Sebald, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 347−358. (f) Tacke, R.; Lopez-Mras, A.; Sperlich, J.; Strohmann, C.; Kuhs, W. F.; Mattern, G.; Sebald, A. *Chem. Ber.* **1993**, *126*, 851−861. (g) Sperlich, J.; Becht, J.; Mühleisen, M.; Wagner, S. A.; Mattern, G.; Tacke, R. *Z. Naturforsch. B* **1993**, *48*, 1693−1706. (h) Tacke, R.; Lopez-Mras, A.; Jones, P. G. *Organometallics* **1994**, *13*, 1617−1623. (i) Tacke, R.; Mühleisen, M.; Jones, P. G. *Angew. Chem.* **1994**, *106*, 1250−1252; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1186−1188. (j) Mühleisen, M.; Tacke, R. *Chem. Ber.* **1994**, *127*, 1615−1617. (k) Mühleisen, M.; Tacke, R. *Organometallics* **1994**, *13*, 3740−3742. (l) Tacke, R.; Mühleisen, M. *Inorg. Chem.* **1994**, *33*, 4191−4193. (m) Tacke, R.; Mühleisen, M.; Lopez-Mras, A.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **1995**, *621*, 779−788. (n) Tacke, R.; Heermann, J.; Pülm, M. *Organometallics* **1997**, *16*, 5648−5652. (o) Pülm, M.; Tacke, R. *Organometallics* **1997**, *16*, 5664−5668. (p) Pfrommer, B.; Tacke, R. *Eur. J. Inorg. Chem.* **1998**, 415−418. (q) Tacke, R.; Heermann, J.; Pülm, M.; Richter, I. *Organometallics* **1998**, *17*, 1663−1668.

(3) Reviews and proceedings dealing with pentacoordinate silicon compounds: (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99−189. (b) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds, Part 1;* Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; pp 227−303. (c) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17−31. (d) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448. (e) Tacke, R.; Becht, J.; Lopez-Mras, A.; Sperlich, J. *J. Organomet. Chem.* **1993**, *446*, 1−8. (f) Wong, C. Y.; Woollins, J. D. *Coord. Chem. Rev.* **1994**, *130*, 175−241. (g) Tacke, R.; Becht, J.; Dannappel, O.; Kropfgans, M.; Lopez-Mras, A.; Mühleisen, M.; Sperlich, J. In *Progress in Organosilicon Chemistry*; Marciniec, B., Chojnowski, J., Eds.; Gordon and Breach Publishers: Amsterdam, 1995; pp 55−68. (h) Tacke, R.; Dannappel, O.; Mühleisen, M. In *Organosilicon Chemistry II From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996; pp 427−446. (i) Tacke, R.; Dannappel, O. In *Tailor-made Silicon Oxygen Compounds From Molecules to Materials*; Corriu, R., Jutzi, P., Eds.; Vieweg: Braunschweig/Wiesbaden, Germany, 1996; pp 75−86. (j) Lukevics, E.; Pudova, O. A. *Chem. Heterocycl. Compd.* **1996**, *353*, 1605−1646. (k) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927−950.

(4) Solution-state ^{29}Si NMR studies with **4−11** (**4−10**, CD_3OD; **11**, CD_3CN) failed. Under the experimental conditions used, no ^{29}Si resonance signals could be detected.

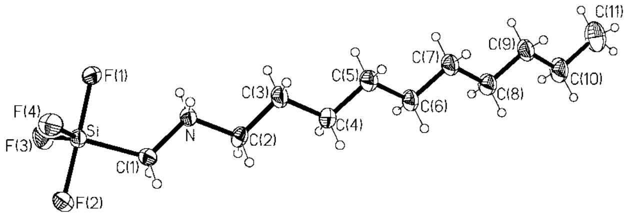

Figure 1. Molecular structure of **8** in the crystal (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analysis of 8

empirical formula	$C_{11}H_{25}F_4NSi$
formula mass, g mol^{-1}	275.41
collcn *T*, K	203(2)
λ(Mo Kα), Å	0.710 73
cryst syst	monoclinic
space group (No.)	$P2_1/c$ (14)
a, Å	19.467(5)
b, Å	8.274(2)
c, Å	9.116(2)
β, deg	97.83(2)
V, Å^3	1454.6(6)
Z	4
D(calcd), g cm^{-3}	1.258
μ, mm^{-1}	0.186
F(000)	592
cryst dimens, mm	0.2 × 0.2 × 0.2
2θ range, deg	4.22−49.98
index ranges	$0 \leq h \leq 22$, $-9 \leq k \leq 0$, $-10 \leq l \leq 10$
no. of collcd reflns	2497
no. of indep reflns	2421
R_{int}	0.0237
no. of reflns used	2421
no. of params	164
S^a	1.048
weight params *a*/*b*^{b}	0.0250/1.0530
$R1^c[I > 2\sigma(I)]$	0.0387
$wR2^d$ (all data)	0.0983
extinction coeff	0.0013(4)
max/min res electron dens, e Å^{-3}	+0.241/−0.220

[a] $S = \{\sum [w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; *n* = no. of reflections; *p* = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = (F_o^2 + 2F_c^2)/3$. [c] $R1 = \sum||F_o| - |F_c||/\sum |F_o|$. [d] $wR2 = \{\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]\}^{0.5}$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 8

Si−F(1)	1.691(2)	Si−F(4)	1.612(2)
Si−F(2)	1.680(2)	Si−C(1)	1.877(3)
Si−F(3)	1.600(2)		
F(1)−Si−F(2)	177.28(10)	F(2)−Si−F(4)	88.69(9)
F(1)−Si−F(3)	90.24(10)	F(2)−Si−C(1)	88.83(11)
F(1)−Si−F(4)	88.59(9)	F(3)−Si−F(4)	117.98(11)
F(1)−Si−C(1)	92.66(11)	F(3)−Si−C(1)	118.22(13)
F(2)−Si−F(3)	91.06(10)	F(4)−Si−C(1)	123.78(13)

the zwitterion **8** in the crystal is shown in Figure 1; selected interatomic distances and angles are listed in Table 2.

Compound **8** crystallizes in the space group $P2_1/c$. The geometry of the coordination polyhedron around the silicon atom of **8** is best described as a slightly distorted trigonal bipyramid, with the carbon atom C(1) and the fluorine atoms F(3) and F(4) in the equatorial positions. In terms of the Berry pseudorotation coordinate, the dihedral angle method[5] shows that the geometry of the coordination polyhedron is displaced by 8% from the ideal trigonal bipyramid toward the ideal square pyramid, with the fluorine atom F(3) as the pivot ligand. As would be expected for a trigonal-bipyramidal SiF_4C coordination polyhedron, the axial Si−F distances [Si−F(1), 1.691(2) Å; Si−F(2), 1.680(2) Å] are significantly longer than the equatorial ones [Si−F(3), 1.600(2) Å; Si−F(4), 1.612(2) Å].

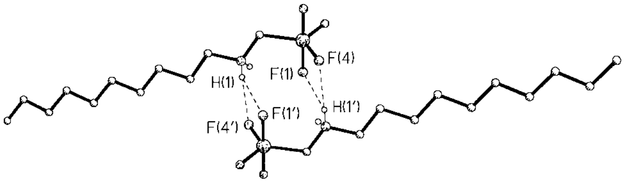

Figure 2. Centrosymmetric dimers of **8** in the crystal. The C*H* hydrogen atoms are omitted for clarity.

Table 3. Geometric Parameters for the Intermolecular Hydrogen Bonds in the Crystal of 8

N···F(1), Å	2.926(3)	N−H(1)···F(4), deg	115(3)
N···F(4), Å	2.934(3)	F(1)···H(1)···F(4), deg	60.1(7)
NH(1)···F(1), Å	2.11(3)	N···F(2), Å	2.936(3)
NH(1)···F(4), Å	2.46(3)	NH(2)···F(2), Å	2.05(3)
N−H(1)···F(1), deg	157(3)	N−H(2)···F(2), deg	160(3)

As expected from the presence of two potential N−H donor functions and four potential fluorine acceptor atoms, N−H···F hydrogen bonds in the crystal of **8** are observed. Considering the relevant geometric parameters (see Table 3), the existence of intermolecular unsymmetric bifurcate N−H(1)···F(1)/N−H(1)···F(4) hydrogen bonds and intermolecular N−H(2)···F(2) hydrogen bonds can be assumed. The bifurcate hydrogen bonds lead to the formation of centrosymmetric dimers of **8** (see Figure 2), which are connected by the N−H(2)···F(2) hydrogen bonds to form infinite layers in the crystal. These layers are characterized by lipophilic surfaces built up by the approximately parallel orientated *n*-alkyl groups of the zwitterions, whereas the polar zwitterionic heads are localized in the middle of these layers. The third dimension of the crystal is built up by stacking these layers.

Acidic Reaction of 4−11 in Aqueous Solution. Compounds **4−11** were found to undergo an acidic reaction in aqueous solution. This phenomenon (not studied in detail) might be explained in terms of a reaction of **4−11** with water to give the corresponding anionic species **4a−11a** and H_3O^+ (Scheme 3). From a formal point of view, addition of the Lewis base OH^- to the pentacoordinate silicon atoms of the Lewis acids **4−11** is analogous to the reaction of the zwitterionic λ^5*Si*-silicate **1** with the isoelectronic F^- ion to yield the anionic λ^6*Si*-silicate **22** (Scheme 4).[3f] The identity of **22** was established by a crystal structure analysis of the corresponding trimethylammonium salt $[HNMe_3][F_5SiCH_2NMe_2H]$.[3f]

pH measurements (glass electrode) with compounds **4** and **11** demonstrated that their aqueous solutions are rather acidic (pH ca. 2−3 at 10^{-1}−10^{-3} mol L^{-1}). To suppress the acidic reaction of **4−11** in aqueous solution (see Scheme 3), the equilibrium surface tension (σ_e) vs concentration (*c*) isotherms of these compounds were always measured in 0.01 M hydrochloric acid.

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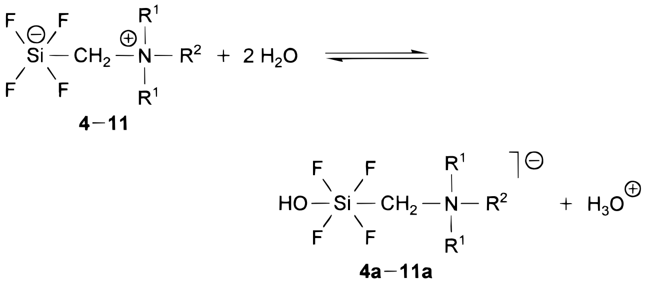
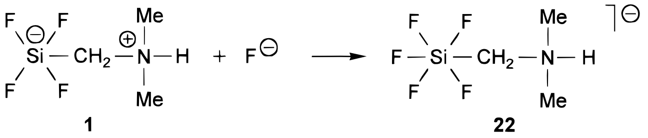
(5) (a) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748−1756. (b) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318−3326. (c) The degree of distortion was calculated by using the dihedral angle method described in ref 5a,b. All nine dihedral angles and the values for the reference geometry of the ideal square pyramid given in ref 5b were considered for this calculation.

Scheme 3



	R^1	R^2
4, **4a**	H	n-C_6H_{13}
5, **5a**	H	n-C_7H_{15}
6, **6a**	H	n-C_8H_{17}
7, **7a**	H	n-C_9H_{19}
8, **8a**	H	n-$C_{10}H_{21}$
9, **9a**	H	n-$C_{11}H_{23}$
10, **10a**	H	n-$C_{12}H_{25}$
11, **11a**	Me	n-C_6H_{13}

Scheme 4



Surface Tension Measurements with Aqueous Solutions of 4−11. The zwitterionic λ^5Si-silicates **4**−**11** were found to be highly efficient surfactants. The lowest surface tension values determined amount to 35−40 mN m^{-1}. Equilibrium surface tension (σ_e) vs concentration (c) isotherms of compounds **4**−**10**, measured in 0.01 M hydrochloric acid (samples used "as synthesized"),[6] revealed a behavior characteristic of homologous series of typical surfactants;[7] i.e., the surface activity was found to increase with increasing n-alkyl chain length. To evaluate the σ_e vs c isotherms quantitatively, a special grade of purity ("surface-chemical purity")[8,9] of the surfactants has to be guaranteed to avoid artifacts caused by highly surface-active trace impurities often being present in surfactants "as synthesized". This particular "surface-chemical purity" was realized for compounds **4** and **11**. For this purpose, aqueous stock solutions of **4** and **11** in 0.01 M hydrochloric acid were purified by an automatically operating high-performance purification apparatus.[10] By this technique, surface-active trace impurities being preferentially enriched at the surface are removed by aspirating the surface periodically in a definite manner until the solution has reached the state of "surface-chemical purity". The progress of this particular purification is illustrated for compound **4** in Figure 3, in which the (apparent) $\bar{\sigma}_e$ values of the solutions under purification are plotted against the number of purification cycles j. The state of "surface-chemical purity" is reached when the differential quotient d$\bar{\sigma}_e$/dj becomes zero.[9] For compounds **4** and **11** ca. 50 to 60 purification cycles were necessary to fulfill this criterion.

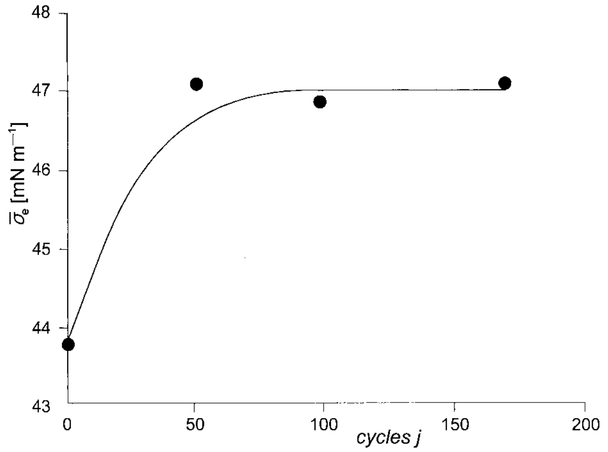


Figure 3. Purification characteristic of a 0.1 M stock solution of **4** measured in 0.01 M hydrochloric acid at 22 °C. The state of "surface-chemical purity" is reached for d$\bar{\sigma}_e$/dj = 0 ($\bar{\sigma}_e$, equilibrium surface tension; j, number of purification cycles); see text.

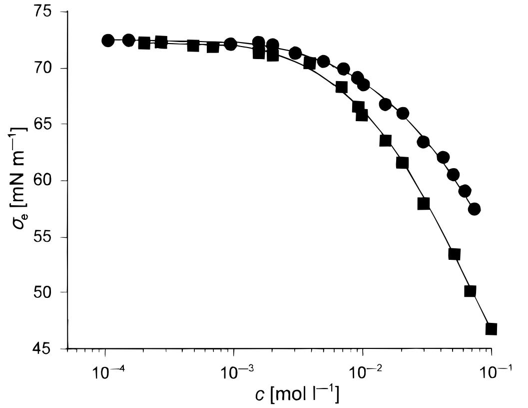


Figure 4. Equilibrium surface tension (σ_e) vs concentration (c) isotherms of solutions of **4** (■) and **11** (●) in 0.01 M hydrochloric acid at 22 °C. (Surfactants were used in the state of "surface-chemical purity"; see text.)

The σ_e vs c isotherms of the purified solutions of the surfactants **4** and **11** (solutions in 0.01 M hydrochloric acid) are shown in Figure 4. As to be expected from basic concepts in surface thermodynamics,[11] a continuously increasing slope with rising concentration was observed. Evaluation of these curves revealed some interesting features. The σ_e vs c isotherms of **4** and **11** can only be matched satisfactorily by a two-state approach of the surface equation of state (for the evaluation of the σ_e vs c isotherms, see refs 12−14; in this context, see also refs 15−18). This characteristic is typical of surfactants, indicating that the adsorption

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(6) The phrase "as synthesized" refers to samples which have been carefully purified by at least three recrystallizations. Nevertheless, the resulting purity does not fulfill the criteria for "surface-chemical purity".

(7) (a) Attwood, D.; Florence, A. T. *Surfactant Systems*; Chapman and Hall: London/New York, 1983. (b) *Cationic Surfactants: Physical Chemistry*; Rubingh, D. N., Holland, P. M., Eds.; Surfactant Science Series, Vol. 37; Marcel Dekker Inc.: New York/Basel, 1991.

(8) Lunkenheimer, K.; Miller, R. *Tenside Deterg.* **1979**, *16*, 312−316.

(9) Lunkenheimer, K.; Miller, R. *J. Colloid Interface Sci.* **1987**, *120*, 176−183.

(10) Lunkenheimer, K.; Pergande, H.-J.; Krüger, H. *Rev. Sci. Instrum.* **1987**, *58*, 2313−2316.

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proceeds via two alternative surface configurations depending on the adsorption density. These two surface configurations can be discriminated by the difference between the corresponding standard free energies of adsorption which were found to be 1.6 kJ mol^{-1} (**4**) and 1.7 kJ mol^{-1} (**11**), respectively.

Although compounds **4** and **11** are characterized by a similar structure (replacement of the NH_2 moiety by an NMe_2 group), a small but noticeable difference in the surface behavior of these surfactants was observed. The surface activity of compound **11** is matched most conveniently by the two-state Henry−Langmuir approach (ideal surface behavior), whereas the properties of **4** can only be matched by the Henry−Frumkin approach (regular surface behavior) although the corresponding surface interaction of about 0.5 kJ mol^{-1} is rather small. Regular surface behavior means attractive interactions between the adsorbed molecules in the interfacial layer. The value for the interaction parameter H^S of about 0.5 kJ mol^{-1} is similar to that observed for *n*-hexanol for which weak hydrogen bonding between the hydroxy groups is assumed.[19] It is likely to assume that intermolecular N−H···F hydrogen bonds (see Crystal Structure Analysis of **8**) are responsible for the regular surface behavior of **4**. As the *N*,*N*-dimethyl derivative **11** does not have N−H functions, it cannot form such hydrogen bonds. According to the calculated cross-sectional areas (see below), the hydrophilic $F_4SiCH_2NH_2$ moiety of **4** and the $F_4SiCH_2NMe_2$ group of **11** are embedded flat in the interfacial layer, with their *n*-hexyl chains orienting upright into the air phase at higher concentrations. Thus, it is feasible that the surface configurations of **4** and **11** are similar to the packing of the zwitterions in the crystal of **8** (see Crystal Structure Analysis of **8**).

The calculated cross-sectional areas $A_{\min}$ of the surfactants **4** and **11** are slightly different. The $A_{\min}$ values amount to 36.2 Å^2 (**4**) and 39.2 Å^2 (**11**) per zwitterion (estimated error ±1 Å^2). This result is in agreement with the different steric requirements of the zwitterions **4** and **11** [replacement of two hydrogen atoms by two methyl groups (**4** → **11**)] and may also reflect intermolecular N−H···F hydrogen bonding in the case of **4** leading to a somewhat denser packing in the interfacial layer.

Finally, it is interesting to note that the surface activity of the zwitterion **4** ($\Delta G_0^{\mathrm{ad}} = -22.1$ kJ mol^{-1}) is a little stronger than that of its *N*,*N*-dimethyl derivative **11** ($\Delta G_0^{\mathrm{ad}} = -20.6$ kJ mol^{-1}). In principle, a weaker surface activity ought to be expected for **4**. However, this unexpected experimental result may be also explained in terms of intermolecular N−H···F hydrogen bonding between the zwitterions **4** in the interfacial layer. Due to these hydrogen bonds, the access of the bulk water molecules to the hydrophilic head of **4** may become somewhat reduced as compared to **11** resulting in a small increase in the surface activity of **4**.

Hydrophobizing Properties of 4−11. When aqueous solutions of compounds **4**−**11** were utilized, hydrophobizing of the glassware (beakers, pipets, containers) was observed. To get some more information about this phenomenon, contact angle measurements with **4** at plane glass plates were performed. For this purpose, cleaned and completely wetted plates were put in a 0.02 M aqueous solution of **4** for 1 h. After the plates were removed from the surfactant solution, they were quickly rinsed with bidistilled water and then dried. Contact angles of a drop of pure water between 82 and 85° were measured at these glass plates. When the glass plates were thoroughly rinsed with streaming tap water, followed by distilled water, and dried again, the remaining contact angles of a drop of pure water were still as high as 53°.

Experimental Section

General Procedures. Except for the reactions with hydrofluoric acid, all syntheses were carried out under dry nitrogen. The solvents used were dried according to standard procedures and stored under nitrogen. The reactions with hydrofluoric acid were carried out in polypropylene or Nalgene beakers under normal atmospheric conditions; for filtrations polypropylene suction flasks, polypropylene Büchner funnels, and normal commercial filter paper were used. Melting points were determined with a Du Pont Instruments differential scanning calorimeter, type Thermal-Analyzer 910. The ^{1}H, ^{13}C, ^{19}F, and ^{29}Si solution-state NMR spectra were recorded at room temperature on a Bruker AMX-400 NMR spectrometer (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{19}F, 376.4 MHz; ^{29}Si, 79.5 MHz). CD_3OD, CD_3CN, and C_6D_6 were used as solvents. Chemical shifts (ppm) were determined relative to internal CD_2HOD (^{1}H, δ 3.30; CD_3OD), CD_3OD (^{13}C, δ 49.00; CD_3OD), CD_2HCN (^{1}H, δ 1.93; CD_3CN), CD_3CN (^{13}C, δ 1.30; CD_3CN), C_6D_5H (^{1}H, δ 7.28; C_6D_6), and C_6D_6 (^{13}C, δ 128.00; C_6D_6) and relative to external TMS (^{29}Si, δ 0) and $CFCl_3$ (^{19}F, δ 0). Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Mass spectra were obtained with a Finnigan MAT-8430 (FAB MS, 3-nitrobenzyl alcohol as liquid matrix, xenon as FAB source), Finnigan MAT-90 (EI MS, 70 eV), or Varian MAT-711 instrument (EI MS, 70 eV). The selected *m*/*z* values given refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{19}F, and ^{28}Si. (Chloromethyl)triethoxysilane (**12**) was purchased from Aldrich.

General Procedure for the Preparation of 4−10. A 48% hydrofluoric acid (1.66 g, 40.0 mmol of HF) solution was added dropwise at 0 °C over 5 min to a stirred solution of the corresponding silanes **13**−**19** (10.0 mmol) in ethanol (80 mL) (first crystals formed after about 15 min). After the reaction mixture was stirred at 0 °C for 2 h and then stored at −20 °C for 20 h, the precipitate was filtered off and recrystallized from ethanol (cooling of a saturated (20 °C) solution to −20 °C) to give compounds **4**−**10** as colorless, crystalline products.

Data for Tetrafluoro[(*n*-hexylammonio)methyl]silicate (4). Yield: 73%. Mp: 107 °C (dec). ^{1}H NMR (CD_3OD): δ = 0.8−0.9 (m, 3 H, CH_3C), 1.3−1.4 (m, 6 H, CCH_2C), 1.5−1.7 (m, 2 H, $NCCH_2C$), 2.41 (s, 2 H, $SiCH_2N$), 2.8−2.9 (m, 2 H, NCH_2C). ^{13}C NMR (CD_3OD): δ = 14.2 (CH_3C), 23.4 (CCH_2C), 27.2 (CCH_2C), 27.3 (CCH_2C), 32.4 (CCH_2C), 37.8 ($SiCH_2N$), 51.4 (NCH_2C). ^{19}F NMR (CD_3OD): δ = −124.8. FAB MS (positive ions): *m*/*z* 200 [100%, M − F$^-$]. FAB MS (negative ions): *m*/*z* 218 [100%, M − H$^+$]. Anal. Calcd for $C_7H_{17}F_4NSi$: C, 38.34; H, 7.81; F, 34.65; N, 6.39. Found: C, 38.3; H, 7.7; F, 34.5; N, 6.4.

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Data for Tetrafluoro[(*n*-heptylammonio)methyl]silicate (5). Yield: 83%. Mp: 122 °C (dec). ^{1}H, ^{13}C, and ^{19}F NMR data and FAB MS data: see Supporting Information. Anal. Calcd for $C_8H_{19}F_4NSi$: C, 41.18; H, 8.21; F, 32.57; N, 6.00. Found: C, 41.2; H, 8.4; F, 32.9; N, 6.0.

Data for Tetrafluoro[(*n*-octylammonio)methyl]silicate (6). Yield: 79%. Mp: 112 °C (dec). ^{1}H, ^{13}C, and ^{19}F NMR data and FAB MS data: see Supporting Information. Anal. Calcd for $C_9H_{21}F_4NSi$: C, 43.70; H, 8.56; F, 30.72; N, 5.66. Found: C, 43.7; H, 8.4; F, 30.9; N, 5.6.

Data for Tetrafluoro[(*n*-nonylammonio)methyl]silicate (7). Yield: 92%. Mp: 110 °C (dec). ^{1}H, ^{13}C, and ^{19}F NMR data and FAB MS data: see Supporting Information. Anal. Calcd for $C_{10}H_{23}F_4NSi$: C, 45.95; H, 8.87; F, 29.07; N, 5.36. Found: C, 45.8; H, 8.7; F, 29.6; N, 5.4.

Data for [(*n*-Decylammonio)methyl]tetrafluorosilicate (8). Yield: 88%. Mp: 127 °C (dec). ^{1}H, ^{13}C, and ^{19}F NMR data and FAB MS data: see Supporting Information. Anal. Calcd for $C_{11}H_{25}F_4NSi$: C, 47.97; H, 9.15; F, 27.59; N, 5.09. Found: C, 48.3; H, 9.2; F, 27.5; N, 5.2.

Data for Tetrafluoro[(*n*-undecylammonio)methyl]silicate (9). Yield: 77%. Mp: 99 °C. ^{1}H, ^{13}C, and ^{19}F NMR data and FAB MS data: see Supporting Information. Anal. Calcd for $C_{12}H_{27}F_4NSi$: C, 49.80; H, 9.40; F, 26.26; N, 4.84. Found: C, 50.0; H, 9.2; F, 26.4; N, 4.9.

Data for [(*n*-Dodecylammonio)methyl]tetrafluorosilicate (10). Yield: 78%. Mp: 147 °C (dec). ^{1}H NMR (CD_3OD): $\delta = 0.8-0.9$ (m, 3 H, CH_3C), 1.2−1.4 (m, 18 H, CCH_2C), 1.5−1.7 (m, 2 H, $NCCH_2C$), 2.40 (s, 2 H, $SiCH_2N$), 2.8−2.9 (m, 2 H, NCH_2C). ^{13}C NMR (CD_3OD): $\delta = 14.4$ (CH_3C), 23.7 (CCH_2C), 27.2 (CCH_2C), 27.6 (CCH_2C), 30.2 (CCH_2C), 30.5 (2 C, CCH_2C), 30.6 (CCH_2C), 30.7 (2 C, CCH_2C), 33.0 (CCH_2C), 37.7 ($SiCH_2N$), 51.4 (NCH_2C). ^{19}F NMR (CD_3OD): $\delta = -123.6$. FAB MS (positive ions): *m/z* 284 [100%, $M - F^-$]. FAB MS (negative ions): *m/z* 302 [100%, $M - H^+$]. Anal. Calcd for $C_{13}H_{29}F_4NSi$: C, 51.45; H, 9.63; F, 25.04; N, 4.62. Found: C, 51.7; H, 9.5; F, 24.8; N, 4.6.

Preparation of Tetrafluoro[(*n*-hexyldimethylammonio)methyl]silicate (11). 1-Bromohexane (1.65 g, 10.0 mmol) was added dropwise at room temperature over 5 min to a stirred solution of **20** (1.79 g, 10.0 mmol) in acetonitrile (20 mL) and the mixture then heated under reflux for 3 h. After the solvent was removed under reduced pressure, the residue was dried in vacuo (0.01 Torr, room temperature, 3 h) to give compound **21** (3.44 g) as a solid crude product. A 48% hydrofluoric acid (1.66 g, 40.0 mmol of HF) solution was added dropwise at 0 °C over 5 min to a stirred solution of **21** (3.44 g, crude product) in ethanol (80 mL) (first crystals formed after about 10 min). After the reaction mixture was stirred at 0 °C for 2 h and then stored at −20 °C for 20 h, the precipitate was filtered off and recrystallized from ethanol (cooling of a saturated (20 °C) solution to −20 °C) to give compound **11** in 86% yield as a colorless crystalline product (2.12 g, 8.57 mmol); mp 129 °C. ^{1}H NMR (CD_3CN): $\delta = 0.9-1.0$ (m, 3 H, CH_3C), 1.3−1.4 (m, 6 H, CCH_2C), 1.6−1.8 (m, 2 H, $NCCH_2C$), 2.79 (s, 2 H, $SiCH_2N$), 3.01 (s, 6 H, NCH_3), 3.2−3.3 (m, 2 H, NCH_2C). ^{13}C NMR (CD_3CN): $\delta = 14.2$ (CH_3C), 23.1 (CCH_2C), 23.6 (CCH_2C), 26.7 (CCH_2C), 31.9 (CCH_2C), 54.1 (NCH_3), 56.6 ($SiCH_2N$), 67.9 (NCH_2C). ^{19}F NMR (CD_3CN): $\delta = -117.1$. FAB MS (positive ions): *m/z* 228 [100%, $M - F^-$]. Anal. Calcd for $C_9H_{21}F_4NSi$: C, 43.70; H, 8.56; F, 30.72; N, 5.66. Found: C, 43.4; H, 8.8; F, 30.8; N, 5.6.

General Procedure for the Preparation of 13−19. A mixture of **12** (100 mmol) and the corresponding *n*-alkylamine (300 mmol) in toluene (200 mL) was heated under reflux for 20 h and then stirred for a further 4 h at room temperature. The precipitate was filtered off, and the solvent and the excess amine were removed under reduced pressure. Then *n*-pentane (200 mL) was added and the mixture stored for 20 h at −20 °C. The precipitate was filtered off and the solvent removed by distillation at normal pressure. The residue was distilled in vacuo (Vigreux column) to give compounds **13**−**19** as colorless liquids.

Data for Triethoxy[(*n*-hexylamino)methyl]silane (13). Yield: 55%. Bp: 60 °C/0.005 Torr. ^{1}H NMR (C_6D_6): $\delta = 0.9$ (br s, 1 H, NH), 0.9−1.0 (m, 3 H, CH_3CC), 1.33 (t, $^{3}J_{HH} = 7.0$ Hz, 9 H, CH_3CO), 1.3−1.6 (m, 8 H, CCH_2C), 2.42 (s, 2 H, $SiCH_2N$), 2.6−2.7 (m, 2 H, NCH_2C), 4.02 (q, $^{3}J_{HH} = 7.0$ Hz, 6 H, CCH_2O). ^{13}C NMR (C_6D_6): $\delta = 14.2$ (CH_3CC), 18.6 (CH_3CO), 23.0 (CCH_2C), 27.4 (CCH_2C), 30.2 (CCH_2C), 32.2 (CCH_2C), 35.1 ($SiCH_2N$), 54.8 (NCH_2C), 58.8 (CCH_2O). ^{29}Si NMR (C_6D_6): $\delta = -50.7$. EI MS: *m/z* 277 [3%, M^+], 206 [100%, $M^+ - C_5H_{11}$]. Anal. Calcd for $C_{13}H_{31}NO_3Si$: C, 56.27; H, 11.26; N, 5.05. Found: C, 56.0; H, 11.0; N, 5.2.

Data for Triethoxy[(*n*-heptylamino)methyl]silane (14). Yield: 58%. Bp: 72 °C/0.005 Torr. ^{1}H, ^{13}C, and ^{29}Si NMR data and EI MS data: see Supporting Information. Anal. Calcd for $C_{14}H_{33}NO_3Si$: C, 57.68; H, 11.41; N, 4.80. Found: C, 57.4; H, 11.2; N, 5.0.

Data for Triethoxy[(*n*-octylamino)methyl]silane (15). Yield: 63%. Bp: 89 °C/0.02 Torr. ^{1}H, ^{13}C, and ^{29}Si NMR data and EI MS data: see Supporting Information. Anal. Calcd for $C_{15}H_{35}NO_3Si$: C, 58.97; H, 11.55; N, 4.58. Found: C, 58.7; H, 11.5; N, 4.8.

Data for Triethoxy[(*n*-nonylamino)methyl]silane (16). Yield: 53%. Bp: 89 °C/0.005 Torr. ^{1}H, ^{13}C, and ^{29}Si NMR data and EI MS data: see Supporting Information. Anal. Calcd for $C_{16}H_{37}NO_3Si$: C, 60.14; H, 11.67; N, 4.38. Found: C, 59.8; H, 11.4; N, 4.6.

Data for [(*n*-Decylamino)methyl]triethoxysilane (17). Yield: 61%. Bp: 98 °C/0.005 Torr. ^{1}H, ^{13}C, and ^{29}Si NMR data and EI MS data: see Supporting Information. Anal. Calcd for $C_{17}H_{39}NO_3Si$: C, 61.21; H, 11.78; N, 4.20. Found: C, 61.4; H, 11.6; N, 4.4.

Data for Triethoxy[(*n*-undecylamino)methyl]silane (18). Yield: 53%. Bp: 109 °C/0.005 Torr. ^{1}H, ^{13}C, and ^{29}Si NMR data and EI MS data: see Supporting Information. Anal. Calcd for $C_{18}H_{41}NO_3Si$: C, 62.19; H, 11.89; N, 4.03. Found: C, 61.8; H, 11.6; N, 4.3.

Data for [(*n*-Dodecylamino)methyl]triethoxysilane (19). Yield: 65%. Bp: 122 °C/0.01 Torr. ^{1}H NMR (C_6D_6): $\delta = 0.9$ (br s, 1 H, NH), 1.0−1.1 (m, 3 H, CH_3CC), 1.3−1.6 (m, 20 H, CCH_2C), 1.33 (t, $^{3}J_{HH} = 7.0$ Hz, 9 H, CH_3CO), 2.42 (s, 2 H, $SiCH_2N$), 2.6−2.7 (m, 2 H, NCH_2C), 4.01 (q, $^{3}J_{HH} = 7.0$ Hz, 6 H, CCH_2O). ^{13}C NMR (C_6D_6): $\delta = 14.3$ (CH_3CC), 18.6 (CH_3CO), 23.1 (CCH_2C), 27.7 (CCH_2C), 29.8 (CCH_2C), 30.04 (CCH_2C), 30.09 (CCH_2C), 30.11 (2 C, CCH_2C), 30.14 (CCH_2C), 30.3 (CCH_2C), 32.3 (CCH_2C), 35.1 ($SiCH_2N$), 54.7 (NCH_2C), 58.7 (CCH_2O). ^{29}Si NMR (C_6D_6): $\delta = -50.4$. EI MS: *m/z* 361 [10%, M^+], 206 [100%, $M^+ - C_{11}H_{23}$]. Anal. Calcd for $C_{19}H_{43}NO_3Si$: C, 63.10; H, 11.98; N, 3.87. Found: C, 63.0; H, 12.1; N, 3.8.

Preparation of [(Dimethylamino)methyl]trimethoxysilane (20). The synthesis was as described in ref 2f.

Crystal Structure Analysis of 8. A suitable air-stable single crystal of **8** was obtained by crystallization from ethanol (cooling of a saturated solution from 40 °C to room temperature). The crystal was mounted on a glass fiber and then transferred to the cold gas stream of the diffractometer (Stoe STADI IV diffractometer, graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å)). Cell parameters were obtained from least-squares fits to the settings of 50 reflections in the range $5° \leq 2\theta \leq 25°$. No significant deviations in intensity were registered for two monitor reflections recorded at regular intervals. No absorption correction was applied. The structure was solved by direct methods.[20] The positions of all nonhydrogen atoms were refined anisotropically.[21] A riding model

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was employed for the refinement of the C*H* hydrogen atom positions. The N*H* hydrogen atoms were localized in difference Fourier syntheses and refined freely.

pH Measurements. pH values of aqueous solutions of **4** and **11** at various concentrations were measured at 22 °C with a pH meter (type WTW 192).

Surface Tension Measurements. Surface tensions of solutions of **4**−**11** in 0.01 M hydrochloric acid were determined at 22 °C with an automatic ring tensiometer (type Lauda) taking into consideration particular modifications necessary for applying it to surfactant solutions.[22] As compounds **4**−**11** produced a strong hydrophobizing of the platinum ring when it was immersed into their aqueous solutions, the resulting measuring error was overcome by relating the measuring values to the measuring reference of pure water according to a procedure described in ref 23.

Contact Angle Measurements. Contact angle measurements with a 0.02 M aqueous solution of **4** were performed at 22 °C using a Zeiss MP 320 apparatus.

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Supporting Information Available: Tables of complete atomic coordinates and U_{eq} values, anisotropic thermal parameters, and additional interatomic distances and angles for **8** as well as NMR and MS data for **5**−**9** and **14**−**18** (7 pages). Ordering information is given on any current masthead page.

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