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ORIGINAL CONTRIBUTION

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Surface activity of amphiphiles in hydrogen fluoride – water solutions

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Abstract Surface tension measurements were carried out in surfactant – hydrofluoric acid – water systems and surfactant – anhydrous hydrofluoric acid systems. Surface tension measurements show that surfactants in anhydrous hydrofluoric acid do not effect a detectable change in surface tension. Effects, known from other solvents, can only be observed when water addition takes place. The surface tension lowering, the free standard adsorption energy, and the maximum surface concentration of a surfactant increases with decreasing hydrofluoric acid concentrations. The space requirement of a separate surfactant molecule decreases at the phase border with decreasing hydrofluoric acid concentrations of the solvents. Simultaneously, the CMC values were changed to smaller surfactant concentrations.

Key words Hydrogen fluoride – surface tension – micelle – surfactant– CMC

Introduction

Only little attention has been pâid to micellation in nonaqueous polar solvents [1 a–k]. Many of these solvents have a high reactivity and high toxicity. But on the other hand, they are excellent solvents for many organic and inorganic compounds, too. Anhydrous hydrogen fluoride belongs to these solvents. The high reactivity of this acid and its high toxicity are the reasons for the difficulties in handling it, and so the aggregation of surfactants in anhydrous hydrogen fluoride and hydrogen fluoride – water solutions has not been well investigated up to now. Only a small number of papers have been published so far [2, 3].

If surfactants are solved in polar solvents they will first occupy the phase border of the solvent. There they build small packed monomolecular films. The hydrophilic group of the surfactant molecule is directed to the polar phase. The hydrophobic tail is directed to the nonpolar phase. The surface tension of the solvent is reduced simultaneously.

The connection between surface tension and surfactant concentration is given by the von Szyskowski equation 1:

$$\Delta\gamma = \gamma_0 - \gamma = A \ln\left(1 + \frac{c}{B}\right), \qquad (1)$$

where $\Delta\gamma$ is decrease of surface tension, γ_0 is surface tension of the pure solvent, γ is surface tension of a solution, c is volume concentration of the surfactant, and A, B are constants of the von Szyskowski equation.

With increasing surfactant concentrations the surface tension decreases as long as the solvent surface is covert monomoleculary. From a determined concentration, the critical micelle concentration (CMC), micellar aggregates are formed inside of the bulk phase. The surface tension does not further decrease [4, 5]. The γ value of such monomolecular layer corresponds to the free surface energy of the hydrophobic tail of the surfactant molecule. If the solubility of the surfactant in the second phase can be neglected, the surface concentration Γ of the surfactant with dependence on the volume concentration can determined by the Gibbs adsorption isotherms (2).

$$\Gamma = -\frac{1}{RT} * \frac{d\gamma}{d\ln c}, \tag{2}$$

where R is the gas constant.

Below the CMC the surface concentration increases to reach its maximum value at the CMC. Evans [6] determined the changes of the free enthalpy of micellation by Eq. (3).

$$\Delta_{\mathrm{M}} G = \Delta G_{(\mathrm{P})} + \Delta G_{(\mathrm{K})} = RT \ln x_{(\mathrm{CMC})}, \tag{3}$$

where $\Delta_{\mathrm{M}} G$ is free micelle formation energy.

In this equation $\Delta G_{(\mathrm{P})}$ represents the change of the free enthalpy by passing over the hydrophobic tail of the molecule from the polar solvent to the nonpolar pseudo phase of the micelle.

The changes in interactions of the hydrophilic head groups are given by $\Delta G_{(\mathrm{K})}$ [6].

The maximum surface concentration Γ_∞ and the space requirement of surfactant molecules at the surface can be determined by the combination of Eqs. (1) and (2) [7, 8].

$$\Gamma_\infty = \frac{A}{RT} \tag{4}$$

$$F = \frac{1}{\Gamma_\infty N_L}, \tag{5}$$

where Γ_∞ is maximum surface concentration, F is space requirement of a surfactant molecule at the surface, and N_L is Avogadro number.

Combination of Eq. (1) with the Langmuir-adsorption isotherm (6) for aqueous systems (7), respectively, opens the possibility to determine the standard free adsorption enthalpy from the von Szyskowski constant:

$$\Gamma = \frac{\Gamma_\infty * x}{x + \exp(\Delta_A G/RT)} \tag{6}$$

$$\Gamma = \frac{\Gamma_\infty * c}{c + 55.5\exp(\Delta_A G/RT)} \tag{7}$$

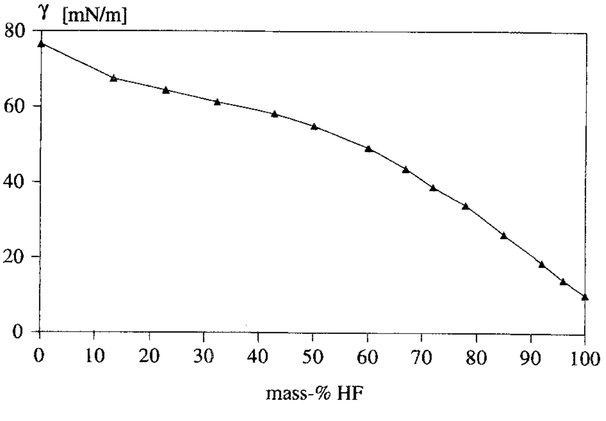
$$B = 55.5\exp(\Delta_A G/RT), \tag{8}$$

where $\Delta_A G$ is free standard adsorption energy.

In consequence of this, Eq. (9) results for hydrofluoric acid – water system:

$$\Delta_A G = RT\ln\frac{B}{c_{\mathrm{H_2O}} + c_{\mathrm{HF}}} \tag{9}$$

Fig. 1 Surface tension of hydrogen fluoride/water-systems in dependence on hydrogen fluoride concentration



Surface tension of hydrofluoric acid solutions in dependence on acid concentration

For hydrofluoric acid – water systems the surface tension could be determined in dependence on the acid concentration at 273 K. As expected the addition of hydrofluoric acid to water leads to a decrease in surface tension of the solution (Fig. 1).

The decrease in surface tension does not turn out to be linear. The surface tension up to 30 mass-% hydrofluoric acid decreases relatively strongly, then up to 60 mass-% only a small decrease is observed. In the range from 60 to 100 mass-% of hydrofluoric acid the surface tension decreases more strongly again. For the surface tension of hydrofluoric acid – water solutions, we found the following equation.

$$\gamma = 76.57 - 0.95c + 2.5*10^{-2}c^2 - 3.3*10^{-4}c^3$$

The surface tension of anhydrous hydrofluoric acid at 273 K determined by Simons and Bouknight is 10.2 mN/m [10]. The surface tension of the hydrofluoric acid used by us was determined to be 11.2 mN/m. The difference of the values depends on the water residue of 0.5%.

Surface activity of sulfobetaines in hydrofluoric acid – water solutions

The interface activity of many surfactants in water has been determined. Our aim was to determine the interface activity of aqueous hydrofluoric solutions. Another point of view was to observe the changes in interface activity with rising hydrofluoric acid concentrations up to anhydrous hydrofluoric acid. For this purpose, we determined the $\gamma/\lg c$ – isotherms of *n*-Dodecyl-dimethylammonio-3-propanesulfonate and *n*-Dodecylammonium chloride in solutions with different hydrofluoric acid concentrations (Figs. 2 and 3).

At hydrofluoric acid concentrations below 38 mass-% measurements could not be carried out, because the solubility of surfactants below this concentration was incomplete.

The adsorption isotherms of the investigated compounds show an analogous course in hydrofluoric acid and water solutions. So, the isotherms can be described by the von Szyskowski equation (1). The CMC is given by the point of intersection of the adsorption isotherm and the regression line of the values above the CMC.

Physicochemical parameters like CMC, A, B, $\Delta\gamma$, Γ_∞, F, $\Delta_A G$, $\Delta_M G$ for different hydrofluoric acid concentrations are given in Table 1.

With increasing hydrofluoric acid concentration the surface tension of the pure solvent decreases and the surface tension lowering by surfactant addition decreases, too. This means that the influence of the surface tension is lowered. That is expressed by a decrease of $\Delta_A G$ with increasing hydrofluoric acid concentrations. The maximum surface concentration is lowered also, but there is a larger space requirement of one separate surfactant molecule on the solvent surface.

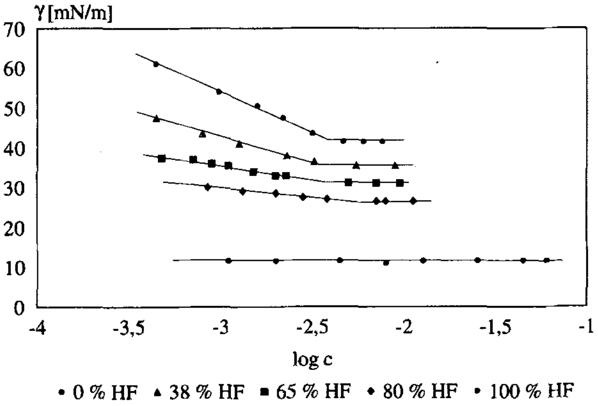
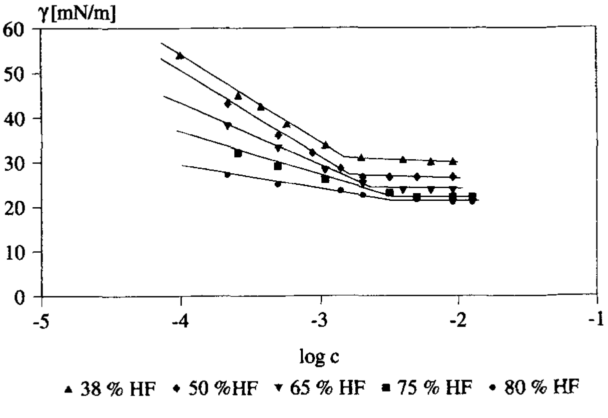


Fig. 2 γ/log$c$-isotherms of n-Dodecyldimethylammonio-3-propanesulfonate with different hydrofluoric acid concentrations ($T = 273$ K)

Fig. 3 γ/log$c$-isotherms of n-Dodecylammonium chloride with different hydrofluoric acid concentrations ($T = 273$ K)



With increasing hydrofluoric acid concentration the CMC is shifted to higher values, though the CMC values lie up to an acid concentration of 40 mass-% in the range of values determined for water.

An addition of surfactants to anhydrous hydrofluoric acid does not lead to a detectable change in surface tension.

Strong changes in surface tension are not expected, because pure liquid hydrogen fluoride exhibits a surface tension of only 10.2 mN/m at $T = 273$ K. The reason for this is the easy break and recombination of zigzag chains of the hydrogen fluoride [11].

However, little changes in surface tension of $(HF)_n$, released by temperature variations, were detectable.

We searched the surface tension of liquid hydrogen fluoride in dependence on the temperature. The obtained data are in good agreement with values found by Simons [10] (Fig. 4).

It follows that surfactants lose their activity in regard to surface tension in anhydrous hydrogen fluoride. The addition of small amounts of water has no effect on it. The well-known influence of surfactants on solvents is observed in hydrogen fluoride solutions at water concentrations above 10 mass-%.

Experimental observations show that surface tension rather will be increased, interfacial tension respectively [12, 13].

Influence of alkyl chain length on surface activity

A dependence of adsorption parameters and CMC values on the alkyl chain length of a series of homologous surfactants can be observed in aqueous hydrofluoric acid solutions, too (Table 2). The CMCs of the investigated surfactants follow the Klevens equation observed in many other solvents. With increasing hydrofluoric acid concentrations the dependence of the CMC on alkyl chain length decreases. The differences in CMC values of short chain surfactants in dependence on the hydrofluoric acid concentration are not as clear, as they are for surfactants with long alkyl chains. The CMC values of surfactants with short chain length (C_{10} and C_{12}) in low concentrated hydrofluoric acid lie below the CMC values determined in pure water (Fig. 5).

An increase of alkyl chain length leads in hydrofluoric acid solutions, like in water and sulfuric acid [14], to

Table 1 Physicochemical parameters of *n*-Dodecyl-dimethylammonio-3-propanesulfonate (DdDAPS) and *n*-Dodecylammonium chloride (DdAHCl) in hydrogen fluoride/water-mixtures ($T = 273$ K)

	HF-%	CMC mol/dm³	A mN/m	B mol/dm³	$\Delta\gamma$ mN/m	Γ_∞ mol/m²	F m²	$-\Delta_A G^\circ$ kJ/mol	$-\Delta_M G$ kJ/mol
DdDAPS	0	3.60E-03	9.02	1.10E-04	31.8	3.97E-06	4.18E-19	32.5	23.9
	38	3.60E-03	4.97	1.00E-04	15.5	2.19E-06	7.58E-19	30	23
	50	3.80E-03	3.52	1.30E-04	10.3	1.42E-06	1.26E-18	29.3	22
	65	4.10E-03	2.23	1.70E-04	7.5	9.82E-07	1.69E-18	28.7	21.1
	75	5.20E-03	1.46	2.30E-04	5.2	5.43E-07	1.54E-17	28.1	20.6
	80	6.50E-03	0.89	2.90E-04	3	3.92E-07	4.24E-17	27.4	19.8
	100	2.90E-02							14.8
	0 [9]	2.30E-03			36.5	3.52E-06	4.72E-19	34.1	24.2
DdAHCl	38	1.50E-03	7.54	5.60E-05	24	3.32E-06	5.00E-19	31.3	23.9
	50	1.80E-03	7.23	8.30E-05	20.2	3.20E-06	5.20E-19	30.2	23.6
	65	2.10E-03	6.87	1.50E-04	15.5	3.03E-06	5.48E-19	29	23
	75	4.00E-03	4.32	4.33E-04	10	1.80E-06	1.03E-18	27.2	21.3
	80	7.00E-03	2.71	1.10E-04	6	1.19E-06	1.38E-18	24.9	20.2

Table 2 Physicochemical parameters of Sulfobetaines in HF-solutions in dependence on alkyl chain length

	HF-%	CMC mol/dm³	A mN/m	B mol/dm³	$\Delta\gamma$ mN/m	Γ_∞ mol/m²	F m²	$-\Delta_A G^\circ$ kJ/mol	$-\Delta_M G$ kJ/mol
DdDAPS	38	2.20E-03	4.97	1.00E-04	15.5	2.19E-06	7.58E-19	30	23
	65	4.70E-03	2.23	1.70E-04	7.5	9.82E-07	1.69E-18	28.7	21.1
	100	2.90E-02							14.8
TdDAPS	38	6.30E-04	7.03	5.28E-05	18	3.10E-06	5.36E-19	31.4	25.8
	65	8.70E-04		1.20E-04	12.3	1.50E-06	1.34E-18	30.2	23.4
	100	1.80E-02							15.9
HdDAPS	38	3.20E-04	9.78	4.23E-05	21	4.31E-06	3.85E-19	32	27.4
	65	5.20E-04		1.10E-04	15.4	2.40E-06	1.03E-18	30.8	25.3
	100	1.00E-02							17.3

DdDAPS = *n*-Dodecyl-dimethylammonio-3-propanesulfonate
TdDAPS = *n*-Tetradecyl-dimethylammonio-3-propanesulfonate
HdDAPS = *n*-Hexadecyl-dimethylammonio-3-propanesulfonate

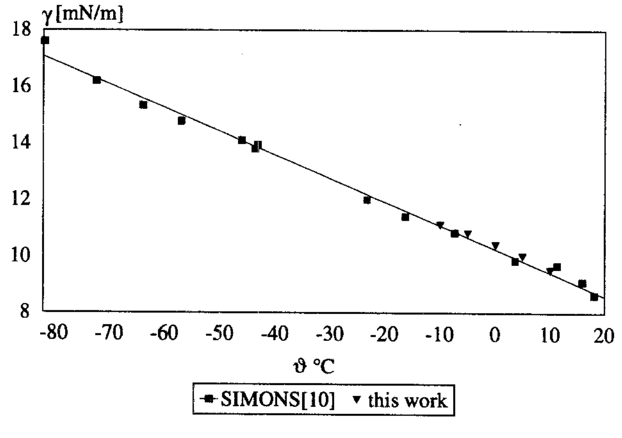


Fig. 4 Surface tension of liquid hydrogen fluoride in dependence on temperature

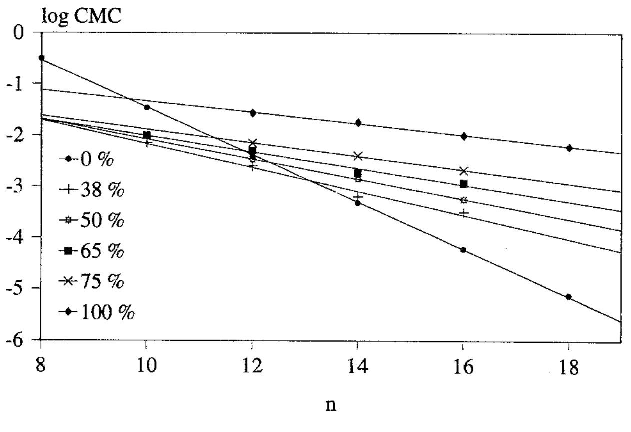


Fig. 5 Klevens-correlations of *n*-Alkyl-dimethylammonio-3-propanesulfonate in dependence on hydrofluoric acid concentrations ($T = 273$ K)

Table 3 Physicochemical parameters in HF-solutions in dependence on the structure of surfactant head group

	HF-%	CMC mol/dm^3	A mN/m	B mol/dm^3	$\Delta\gamma$ mN/m	Γ_∞ mol/m^2	F m^2	$-\Delta_A G^\circ$ kJ/mol	$-\Delta_M G$ kJ/mol
DdAHCl	38	1.5	7.54	5.60E-05	24	3.32E-06	5.00E-19	31.3	23.9
	65	2.1	6.87	1.50E-04	15.5	3.03E-06	5.48E-19	29	23
DdABS	38	2.2	5.73	6.00E-05	22	2.50E-06	6.58E-19	31.2	22.5
	65	4.3	3.9	1.56E-04	9.8	2.10E-06	8.02E-19	28.6	19.8
	100	33							14.6
DdTABr	38	2.1	5.43	8.30E-05	17.3	2.30E-06	7.20E-19	30.6	21.5
	65	4.5	3.1	1.62E-04	8.2	1.80E-06	1.27E-18	28.7	19.6
DdDAPS	38	2.2	4.97	9.85E-05	15.5	2.19E-06	7.58E-19	30	23
	65	4.7	2.23	1.69E-04	7.5	9.82E-07	1.69E-18	28.7	21.1
	100	29							14.8

DdAHCl = *n*-Dodecylammonium chloride
DdABS = *n*-Dodecylammonio-4-butanesulfonate
DdTABr = *n*-Dodecyl-trimethylammonium bromide
DdDAPS = *n*-Dodecyl-dimethylammonio-3-propanesulfonate

higher surface tension lowering and higher maximum surface tension. The absorption energy was also increased and the space requirement of a surfactant molecule on the phase border was decreased as well. Changes in physicochemical parameters in hydrofluoric acid are not as significant as in other solvents (Table 2).

Influence of surfactant head group structure on surface activity

The physicochemical parameters of the following surfactants are compared to determine the influence of surfactant head group structure on the adsorption behavior on the phase border.

$C_nH_{2n+1}\text{–}NH_2^+\text{–}(CH_2)_4\text{–}SO_3^-$

$C_nH_{2n+1}\text{–}N^+(CH_3)_2\text{–}(CH_2)_3\text{–}SO_3^-$

$C_nH_{2n+1}\text{–}NH_3^+Cl^-$

$C_{14}H_{29}\text{–}N^+(CH_3)_3Br^-$

The parameters of these compounds are given in Table 3.

Solvent surface tension lowering decreases during addition of a surfactant in the following line:

$$R\text{–}NH_3^+Cl^- > R\text{–}NH_2^+\text{–}(CH_2)_4 - SO_3^-$$
$$> R\text{–}N^+(CH_3)_3Br >$$
$$R\text{–}N^+(CH_3)_2\text{–}(CH_2)_3\text{–}SO_3^-$$

In the same order the maximum surface concentration decreases, during the space requirement of a surfactant molecule at the phase border increases. The $\Delta_A G$ values show only small differences. Surfactants with sulfobetaine structure can be arranged well in this line, because they will be protonated in HF solvents and lie before as cationic surfactants. The *n*-alkylammonium salts and *n*-alkylammonio-butanesulfonic acids possess the possibility to develope hydrogen bridge bonds to hydrofluoric acid and water molecules of the solvent. The simultaneous decrease of the positive head group charge reduces the electrostatic repulsion, so that the surface concentration can increase at the phase border.

Micellation in the hydrofluoric acid – water system

The presented sulfobetaines and *n*-alkylammonium salts do not effect a change in the surface tension of the solvent in hydrofluoric acid. A criterion for micellation, the decrease in surface tension during surfactant addition up to the CMC, for anhydrous hydrofluoric acid does not apply.

The suggestion derived from the fact that micellation in anhydrous hydrofluoric acid does not occur, was earlier disproved by us [15–17] and Miethchen and co-workers [18, 19].

A structural probe for micellation is the cohesive energy density (c.e.d.) of the solvent derived by Hildebrand [20, 21] and the Gordon parameter $\gamma/V^{1/3}$ [22]. The Gordon parameter for hydrogen fluoride at 0 °C is given to be 3.7 erg/cm. This value is irrelevant for polar solvents and can be traced back to the very small surface tension of the hydrogen fluoride. That is why the determination of the cohesive energy density is made with the Hildebrand equation [23, 24].

For the hydrogen fluoride – water system the dependence of c.e.d. on the hydrogen fluoride concentration is shown in Fig. 8. The cohesive energy density is determined from enthalpy data of Vieweg [25] (Table 4 and Fig. 6).

The hydrogen fluoride – water system shows a maximum of c.e.d. at a hydrogen fluoride concentration of 54 mass-%. At higher HF concentrations the values for c.e.d.

Table 4 Cohesive energy density of water/hydrogen fluoride-systems, calculated from enthalpy data ($T = 292.6$ K)

Weight-% HF	c.e.d. J/cm^3	$\Delta_v H$ [25] J/mol
0	2409.1	45672.5
10	2549.5	46664.7
20	2653.8	47523.9
30	2754.8	48238
40	2820.4	48367.5
50	2870.6	47930.7
60	2880.9	46786.2
70	2719.4	44067.8
80	2452.1	40519.4
90	2016.3	35800.6
100	1333	28163.8

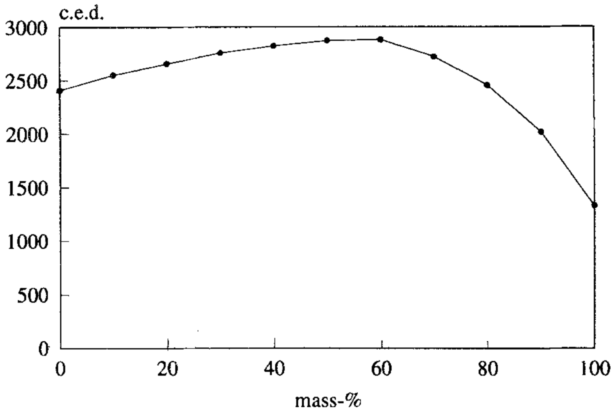


Fig. 6 Cohesive energy density of water/hydrogen fluoride-systems in dependence on hydrofluoric acid concentrations

decrease strongly, to give 1333 J/cm at anhydrous hydrogen fluoride.

Peters and Miethchen [2] published for anhydrous hydrogen fluoride a c.e.d. value of 1332 J/cm. For micellation Zana [26] proposed the lower border of c.e.d. at 1280 J/cm.

The maximum of energy density in the hydrogen fluoride – water system is given by the density maximum and boiling point maximum. These maxima are also an expression for increased hydrogen bridge bonds. The solvatation ability of the solution is also increased for surfactants in this concentration range.

The CMC data of surfactants with short alkyl chains obtained by surface tension measurements are up to a hydrofluoric acid concentration of 60% smaller than those determined in water. Only at higher acid concentrations did CMC values increase strongly. Simultaneous hydrofluoric acid acts by the addition of water as electrolytic additive, because it dissociates in aqueous solution in conformity with the following equation [27].

$$H_2O + HF \rightarrow H_3O^+ + F^- .$$

Therefore, electrolytic additives decrease the repulsive electrostatic interactions between the surfactant head groups and the CMC, too. The three-dimensional structure of water will be broken at higher hydrofluoric acid concentrations and the two-dimensional structure of hydrofluoric acid preponderates. The CMC values are shifted to significant higher surfactant concentrations. The dependence of CMC values on hydrofluoric acid concentration is presented in Fig. 7 with the example of *n*-Dodecyl-dimethylammonio-propanesulfonates.

The CMC of surfactants decisively depends on the strength and number of hydrogen bridge bonds of the solvent. A comparison of CMC data of *n*-Hexadecyl-trimethylammonium bromide in different polar solvents supports this assumption (Table 5).

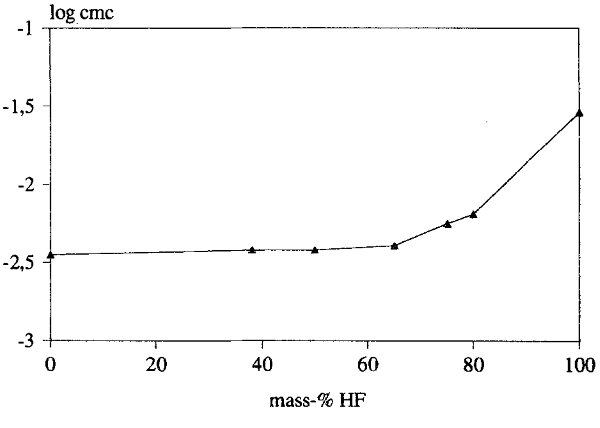
Experimental part

The surface tension measurements could not be carried out in the presence of hydrogen fluoride with methods usually used for aqueous systems. The reason is that hydrogen fluoride and its aqueous solutions react very strongly with many metals and other materials. For the

Table 5 CMC data of *n*-Hexadecyl-trimethylammonium bromide in different polar solvents

Polar solvent	CMC in mol/dm^3	T in K	References
Water	8.00E-04	303	[28]
Sulfuric acid	2.60E-03	291	[14]
Methansulfonic acid	5.71E-02	294	[14]
Hydrofluoric acid	2.40E-02	273	[12]

Fig. 7 CMC-data of *n*-Dodecyl-dimethylammonio-3-propane-sulfonate in dependence on hydrogen fluoride content of hydrofluoric acid/water-solutions



determination of the surface tension, we used a method published by Simons and Bouknight [10]. The principle of measurement is the determination of the maximum pressure necessary to form a gas bubble with defined radius inside of the solvent. This pressure is proportional to the surface tension of the liquid in opposition to the gas.

$$\gamma = (P - D * h * g) * \frac{r}{2},$$

where γ represents the surface tension of the solvent, P the measured pressure at the moment the gas bubble tears off, D the density of the solvent, h the depth of immersion of the capillary into the solvent, g the gravitational acceleration, and r the radius of the capillary.

First the gas is conveyed through a capillary with a large radius up to the moment the gas bubble is torn off. The pressure necessary had been determined. According to that, the gas is conveyed through a capillary with small radius and the pressure needed to form a bubble is determined again. From the pressure difference the surface tension can be determined by using the equation of Sugden [29].

$$\gamma = K * P * (1 + 0{,}69 * r_2 * g * \frac{D}{P},$$

where γ represents the surface tension, K a constant for the equipment, g the gravitational acceleration, P the pressure difference, r_2 the radius of the larger capillary, and D the density of the solvent. The constant K can be determined by calibration of the equipment with water and benzene beyond a broad temperature range. The density of the solvent is constant for a given temperature and the changes in density during surfactant addition is neglected. The measurements were carried out at a temperature of 273 K. To minimize errors, equipment changes made by Cany et al. [30] have been considered. The determination of acid concentration were carried out up to 85 mass-% by alkalimetric titration. Higher acid concentrations were determined by Karl–Fischer-titration.

The construction materials used in the apparatus were polytrifluorochlorethylene and silver for the capillaries.

The stability of the surfactants was controlled by ^{1}H-, and ^{13}C-NMR measurements. No changes in spectra were detectable after treatment of the surfactants with anhydrous or dilute hydrofluoric acid.

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