

# Adsorption of Aminefluorides onto Glass and the Determination of Surface Free Energy, Zeta Potential and Adsorbed Layer Thickness\*

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## ABSTRACT

Aminefluorides are known to affect bacterial adhesion to enamel. In order to obtain information on the structure of adsorbed aminefluoride coatings, dihydroaminefluoride (AmF 297) and oleylaminefluoride (AmF 335) were adsorbed onto glass from solutions with concentrations up to 10 mM. Surface tensions of the solutions were measured at 25°C. After coating the glass surfaces, surface free energies, zeta potentials and adsorbed layer thicknesses were determined from contact angles, electrophoresis and ellipsometry, respectively. Surface free energies decreased after coating with both types of aminefluoride from 109 to ~45 mJ m<sup>-2</sup>. Coating with only high concentrations (> 5 mM) of AmF 297 again resulted in surface free energies above 100 mJ m<sup>-2</sup>. Zeta potentials, originally -45 mV, became positive after coating with both types of aminefluoride (approximately +5 mV). Coating with only AmF 297 at concentrations above 5 mM gave zeta potentials of +20 mV. Adsorbed layer thicknesses were in the monolayer range, though AmF 297 on its own clearly formed thicker layers at higher concentrations. Both surfactants showed a tendency to form micelles in solution at concentrations higher than 1 mM. The results indicate that both aminefluorides adsorb with the positively charged, polar group towards the glass, but only AmF 297 can form double layers at higher concentrations. The second layer, however, adsorbs with the positively charged polar groups towards the solution and is bound to the first layer by relatively weak forces between the hydrocarbon chains. Gentle rinsing with distilled water is sufficient to remove the double layers. This paper shows how a combination of surface techniques can yield a detailed picture of the structure and orientation of adsorbed layers on solid substrata.

## INTRODUCTION

Surfactants have an enormous range of applications in industrial processes from the dewatering of froth-floated coal [1] to the protection of human teeth against bacterial attacks by surfactant adsorption from toothpaste slurries [2].

\*Dedicated to the memory of Professor E. Wolfram.

Primary ( $R-NH_2$ ) and secondary ( $R-NH-R'$ ) amines as well as diamines ( $R-NH-R'-NH_2$ ) have some very interesting and important surface-active properties. Recent work [1] on the effects of oleyldiamine addition to coal slurries showed an increase in the zeta potential of coal particles from  $-35$  to  $+30$  mV upon the addition of only 14 kg oleyldiamine to a tonne of slurry. Simultaneously, receding water contact angles on the coal increased from  $20$  to  $60^\circ$ , with an maximum of  $70^\circ$  at about the point of zero charge of the particles.

Solutions of dihydroaminefluoride and oleylaminefluoride have been found to be highly effective in reducing the formation of dental plaque, the main cause of tooth decay [3]. In vitro determination of the surface free energy of human enamel after adsorption of these aminefluorides indicated a decrease from  $88$  to  $62$   $mJ\ m^{-2}$  [2], which could explain their plaque reducing influence thermodynamically [4].

In the present work, surface free energies, zeta potentials and adsorbed layer thicknesses on glass are determined, after adsorption of dihydroaminefluoride and oleylaminefluoride from solutions with varying surfactant concentrations (up to  $10$  mM). The surface tensions of the solutions were also determined to study possible intermolecular interactions of aminefluoride molecules in the solution phase.

## MATERIALS AND METHODS

### *Preparation of glass substrata*

Chance Cover glass slips (Smethwick, England) were cleaned as follows:

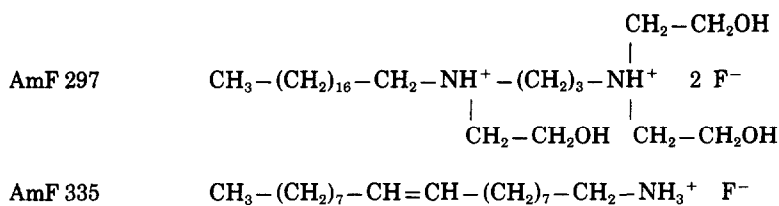
- (i) 24 h in a 1% dodecyl sulphate solution;
- (ii) rinsed 3 times in distilled water;
- (iii) 1 h in a 100 mM HCl solution;
- (iv) rinsed 3 times in distilled water.

The dried glass slips were subsequently put in the aminefluoride solutions (up to  $10$  mM) for 2 min at a volume to area ratio of 20 cm. Dihydroaminefluoride (from now on designated as AmF 297) and oleylaminefluoride (AmF 335) were kindly provided by GABA, Basel, Switzerland. The structural formulae of the aminefluorides employed are summarized in Table 1. After drying, the coated slips were used for surface free energy determinations and measurements of the adsorbed layer thicknesses.

For the zeta potential measurements, the cleaned glass slips were crushed and ground in a stainless-steel ball mill. Particles were sieved in a subsieve sizer yielding particles of  $\sim 5$   $\mu m$  in diameter. After sieving, the particles were washed four times in distilled water and suspended in the various solutions for 2 min with slight agitation. The coated particles were finally suspended in  $10$  mM potassium phosphate (pH 7.0).

TABLE 1

Structural formulas of dihydroaminefluoride (AmF 297) and oleylaminefluoride (AmF 335)

*Surface free energy determinations*

Surface free energies were estimated from advancing contact angles of water (atomic absorption quality), water/n-propanol (Merck, Darmstadt, West Germany, analytical grade) mixtures and  $\alpha$ -bromonaphthalene (Merck, Darmstadt West Germany, analytical grade), employing the concept of dispersion and polar components accounting for the influence of spreading pressures [5,6]. Contact angles were fitted to the geometric mean equation

$$\cos \theta = -1 + 2 (\gamma_s^d \cdot \gamma_1^d)^{1/2} \cdot \gamma_1^{-1} + 2 (\gamma_s^p \cdot \gamma_1^p)^{1/2} \cdot \gamma_1^{-1} - \pi_e \cdot \gamma_1^{-1} \quad (1)$$

where  $\theta$  is the contact angle,  $\gamma_1^d$  and  $\gamma_1^p$  are the (known) dispersion and polar components of the liquid surface tension  $\gamma_1$ ,  $\gamma_s^d$  and  $\gamma_s^p$  are the dispersion and polar components of the solid surface free energy  $\gamma_s$  (to be calculated), and  $\pi_e$  is the equilibrium spreading pressure.

This method has been shown to be extremely suitable for estimating solid-air surface free energies  $\gamma_s$  of low energy substrata such as polytetrafluorethylene ( $\gamma_s \approx 20 \text{ mJ m}^{-2}$ ) as well as of high energy substrata such as glass ( $\gamma_s = 109 \text{ mJ m}^{-2}$ ). All surface free energies reported were determined at  $25^\circ\text{C}$  on five different glass slips.

*Zeta potential measurements*

Zeta potentials were determined at  $25^\circ\text{C}$  in a potassium phosphate buffer (10 mM, pH 7.0, density  $10^8 \text{ particles cm}^{-3}$ ) with a Lazer Zee Meter (Penkem Inc., Bedford Hills, NY) using a potential difference between the electrodes of 150 V. Zeta potentials were calculated from the particle velocity employing the Helmholtz-Smoluchowski equation [5].

*Measurements of adsorbed layer thicknesses*

The thickness of the adsorbed layer was determined ellipsometrically [7]. For adsorbed layers smaller than the wavelength of the incident light the Drude approximation gives

$$\delta\Delta = \Delta - \bar{\Delta} = -\zeta s \quad (2)$$

where  $\Delta$  is one of the ellipsometer parameters ( $\bar{\Delta}$  refers to the clean substratum),  $s$  is the adsorbed layer thickness and  $\zeta$  is a function of the complex refractive indices of the surrounding medium, the adsorbed film and the substratum, the wavelength of the incident light (6328 Å) and the angle of incidence (55.33°). From Eqn. (2) it can be seen that  $\delta\Delta$  is directly proportional to the adsorbed layer thickness. Both ellipsometer parameters  $\bar{\Delta}$  and  $\bar{\psi}$  were measured to calculate the complex refractive index of the glass in order to check whether the surfaces were clean. The polarizer and the analyzer readings were measured within 0.02 degrees resulting in an accuracy in  $\Delta$  and  $\psi$  of 0.04 and 0.02 degrees, respectively.

### *Surface tension measurements of the aminefluoride solutions*

The surface tensions of the aminefluoride solutions were measured at 25°C using a Lauda Autotensiomat (Königshofen, West Germany). Measurements were carried out using a Du Nouy ring (circumference 6 cm) correcting for the Harkins–Jordan factor. The accuracy of the reported surface tensions is  $\pm 0.5$  mJ m<sup>-2</sup>.

## RESULTS

In Table 2 a selection of the contact angles measured on the various substrata is given.

Figure 1 presents the estimated surface free energy of the glass after adsorption of aminefluorides as a function of surfactant concentration. The surface free energy of the clean glass was extremely high (109 mJ m<sup>-2</sup>) indicating that the glass was very clean. Adsorption of both AmF 297 and AmF 335 shows a rapidly decreasing surface free energy with surfactant concentration. Surprisingly, AmF 297 gives high values upon adsorption at concentrations above 5 mM, whereas AmF 335 renders low surface free energies at higher concentrations.

Figure 2 presents the zeta potential of crushed glass slips after adsorption of aminefluorides as a function of surfactant concentration. Both aminefluorides give an initial increase from -45 mV to +5 mV, followed by a steep increase at about 1 mM. The zeta potential of AmF 297 coated glass particles continuously increases with increasing concentration, whereas the zeta potential of AmF 335 coated glass remains at +7 mV for all concentrations above 2 mM.

Figure 3 presents the adsorbed layer thickness (in relative units) as a function of the AmF concentration in solution. The clean surface values  $\bar{\Delta}$  and  $\bar{\psi}$ , 175.1 and 2.1, respectively, result in a complex refractive index  $\bar{n} = 1.52 - i \times 0.006$ , in agreement with the literature [8]. The adsorbed layer

TABLE 2

Water and  $\alpha$ -bromonaphthalene ( $\alpha$ -br) contact angles (degrees) on glass slips after adsorption of AmF 297 and AmF 335 as a function of the surfactant concentration

$C$ (mM)	AmF 297		AmF 335	
	$\theta_{\text{H}_2\text{O}}$	$\theta_{\alpha\text{-br}}$	$\theta_{\text{H}_2\text{O}}$	$\theta_{\alpha\text{-br}}$
0.0	25	31	25	31
0.02	49	32	38	33
0.1	53	33	54	38
0.2	63	39	67	40
0.5	74	44	73	48
0.8	68	39	64	46
1.0	70	43	77	47
1.2	73	39	77	45
1.5	68	43	83	46
2.0	68	44	74	42
3.5	79	41	85	48
5.0	64	40	67	46
10.0	34	38	70	43

thickness initially increases ( $\delta\Delta \sim -2^\circ$ ), showing a continued increase at about 2 mM for both aminefluorides, which is, however, more pronounced for AmF 297 than for AmF 335.  $\delta\Delta$  for AmF 297 at high concentrations doubles ( $2 < c < 5$  mM) with respect to the lower concentrations ( $0.5 < c < 2$  mM) and even amounts to  $-9^\circ$  at  $c = 10$  mM, at which concentration AmF 335 is only  $-4^\circ$ .

Absolute values for the adsorbed layer thickness can be obtained by assuming a refractive index for the adsorbed film. Refractive indices of 1.3 or 1.45 yield  $\zeta$  values [see Eqn (2)] of  $0.26$  and  $0.12^\circ \text{ \AA}^{-1}$ , respectively, from which an absolute value for the adsorbed layer thickness may be calculated.

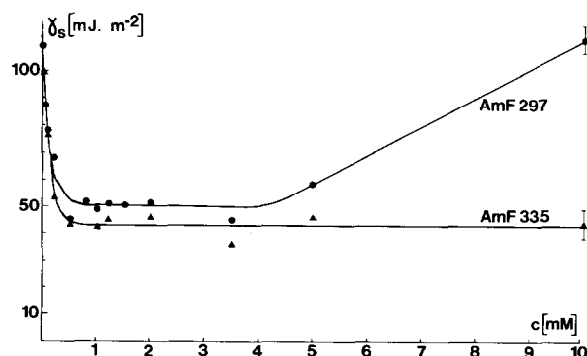


Fig. 1. Surface free energies  $\gamma_s$  of glass after adsorption of aminefluorides from solutions with various surfactant concentrations  $C$ . The bars denote the standard deviation over five glass slips.

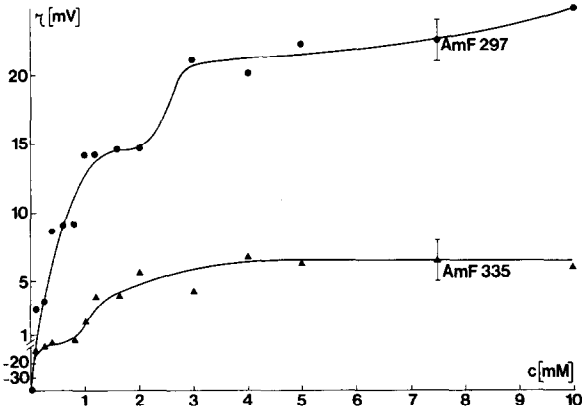


Fig. 2. Zeta potentials  $\zeta$  of glass after adsorption of aminefluorides from solutions with various surfactant concentrations  $C$ . The bars denote the standard deviation over six independent observations.

Surface tensions of the solutions, presented in Fig. 4, show a tendency of the aminefluorides to form micelles at concentrations above 1 mM.

## DISCUSSION

The results of this study show that the physico-chemical properties of glass can be drastically altered by aminefluoride adsorption. A comparison of the concentration dependence of  $\gamma_s$ ,  $\zeta$  and  $\delta\Delta$  (Figs 1–3) makes it possible to form a detailed picture of the structure and orientation in the adsorbed aminefluoride layer. The completion of the first monolayer occurs at very low concentrations ( $< 1$  mM): surface free energies decrease to a low value (Fig. 1), zeta potentials show an increase (Fig. 2) and the adsorbed layer thickness shows a

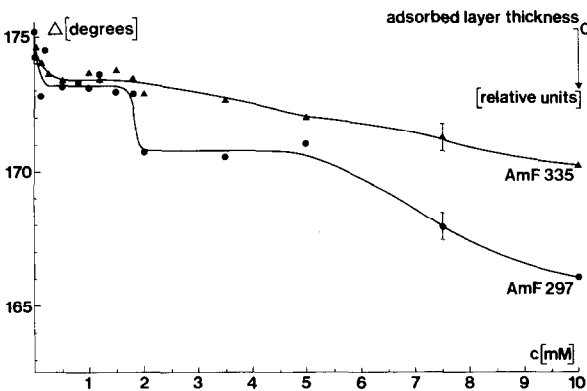


Fig. 3. Adsorbed layer thicknesses of aminefluorides adsorbed on glass as a function of the surfactant concentration  $C$  in solution. The bars denote the standard deviation over five glass slips.

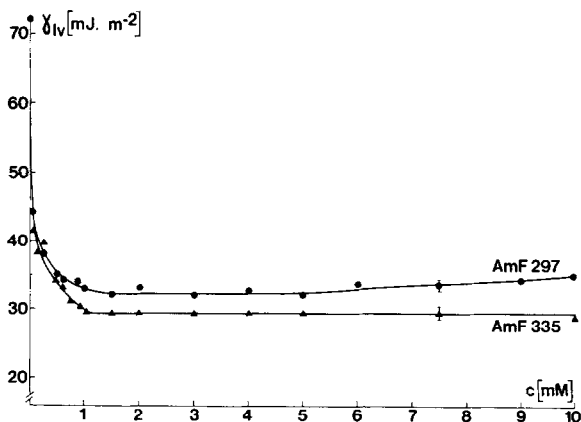


Fig. 4. Surface tensions  $\gamma_{lv}$  of aminefluoride solutions as a function of aminefluoride concentration  $C$  measured at 25°C. The bars denote the experimental accuracy

plateau value (Fig. 3), corresponding to a layer thickness between 15 and 35 Å, if a refractive index of the adsorbed film between 1.3 and 1.45 is assumed. Simultaneously, molecules start to form micelles in solution at about 1 mM (Fig. 4).

The surface free energy of AmF 335 coated glass remains low ( $\approx 45 \text{ mJ m}^{-2}$ ) if the concentration in solution is increased, while the zeta potential as well as the adsorbed layer thickness increase only very slowly with concentration. It is probable that the density of adsorbed molecules at the surface increases, but no double layers are formed.

Double layer formation of adsorbed AmF 297 is indicated by the changes in surface free energy and zeta potential as well as in adsorbed layer thickness at concentrations above 1 mM (Figs 1–3). The positively charged polar groups of this second layer will be directed towards the solution, as is indicated by the fact that the surface free energy increases again above 1 mM (Fig. 1) and that the zeta potential increases to +20 mV (Fig. 2).

The broad outlines of the structure and orientation in the adsorbed films laid out above should be considered with some caution. The long hydrocarbon chains (long compared with the polar head) may take several other configurations, all more or less compatible with the experimental results [9]. Basically, however, we believe the overall picture presented to be sound.

The binding between the positively charged polar groups of the aminefluorides and the glass surface was relatively strong. Rinsing the coated glass slips with distilled water hardly changed the measured surface characteristics of AmF 335 coated glass (see Table 3). It appeared to be easy, however, to remove the double layers of AmF 297, formed in the region between 2 and 10 mM as after rinsing only once with distilled water the surface characteristics of the glass, coated with 5 and 10 mM AmF 297 solutions, resembled the characteristics of glass with an adsorbed monolayer of AmF 297, while the surface char-

TABLE 3

The influence of rinsing the glass slips with adsorbed aminefluorides in distilled water upon water and  $\alpha$ -bromonaphthalene contact angles, surface free energy, zeta potential and adsorbed layer thickness (expressed as the ellipsometer parameter  $\delta d$ )

Surfactant	Concentration (mM)	Without rinsing					With rinsing				
		$\theta_{\text{H}_2\text{O}}$ ( $^\circ$ )	$\theta_{\alpha\text{-br}}$ ( $^\circ$ )	$\gamma_s$ ( $\text{mJ m}^{-2}$ )	$\zeta$ (mV)	$\delta d$ ( $^\circ$ )	$\theta_{\text{H}_2\text{O}}$ ( $^\circ$ )	$\theta_{\alpha\text{-br}}$ ( $^\circ$ )	$\gamma_s$ ( $\text{mJ m}^{-2}$ )	$\zeta$ (mV)	$\delta d$ ( $^\circ$ )
AmF 297	1	70	43	50	14.1	-2.1	70	43	51	14.0	-1.5
	5	64	40	59	22.1	-4.2	64	40	58	16.9	-1.1
	10	34	38	116	24.7	-9.2	67	41	55	16.7	-1.9
AmF 335	1	77	47	42	2.0	-1.6	68	44	49	2.0	-1.6
	5	67	46	46	6.2	-3.3	67	46	46	5.6	-2.0
	10	70	43	45	5.9	-5.1	82	45	31	5.0	-1.2

acteristics of the glass, coated with 1 mM AmF 297 solution, hardly changed when rinsed (see Table 3).

It is difficult to understand why AmF 335 does not share AmF 297's ability to form adsorbed double layers. It is probable that the ability of AmF 297 to form double layers will be enhanced by the second amine group in the hydrocarbon chain and the two hydroxylgroups in the polar head of the molecule (see Table 1).

Double-layer formation of aminefluorides adsorbed on ground and polished human enamel has been suggested previously by De Jong et al. [2] on the basis of experiments in which the surface free energy of enamel was determined as a function of adsorption time at fixed aminefluoride concentration in a commercially available solution (Elmex Fluid, GABA, Basel Switzerland), containing both AmF 297 and AmF 335. In this study too, the adsorbed double layers could be removed by rinsing with distilled water.

In conclusion, it can be stated that with a combination of surface techniques it is possible to obtain a detailed picture of the structure and orientation in adsorbed layers on solid substrata, as demonstrated by studying the adsorption of two types of aminefluorides on glass.

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