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Structural insight into the interactions between a cationic dye and an anionic surfactant in crystals of 9-aminoacridinium dodecyl sulfate

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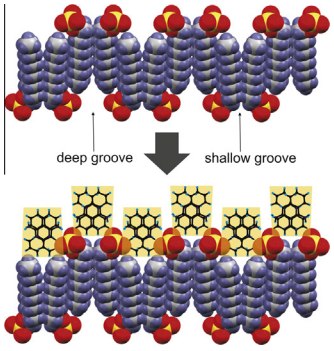
HIGHLIGHTS

- 9-Aminoacridinium dodecyl sulfate was synthesized and structurally characterized.
- A new type of self-assembled monolayer of dodecyl sulfate in the crystals was identified.
- An analysis of the dye-surfactant interactions in the crystal packing was carried out.

GRAPHICAL ABSTRACT



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ABSTRACT

9-Aminoacridinium dodecyl sulfate, a salt consisting of a cationic dye and an anionic surfactant, was synthesized and structurally characterized. In the crystal packing, dodecyl sulfate anions interact via weak C–H···O hydrogen bonds and van der Waals interactions to form monolayers. These monolayers have a corrugated surface in which shallow and deep grooves are distinguishable. 9-Aminoacridinium cations form π-stacking columns, which are located in these grooves, and interact with dodecyl sulfate monolayers via N–H···O and C–H···O hydrogen bonds. The monolayers of dodecyl sulfate ions observed in the crystal structure of the title compound represent a new type of self-assembled monolayers of this surfactant in the crystals.

Introduction

Acridine dyes have long occupied a special place in many fields of research. This is due not only to their staining and photosensitisation abilities, which are commonly applied in studies of various biological [1–6] and physicochemical systems [7–11]. Acridines also exhibit a wide range of therapeutic activities, e.g. antibacterial [12], anticancer [13], antiprion [14] and antiviral [15] properties. For these reasons, much attention has been given in recent years to the interactions between acridine dyes and surfactants. Studies concerning dye-surfactant interactions may be helpful for gaining a better understanding of molecular recognition processes [16,17]. Interactions between cationic dyes and anionic surfactants in solution, where different types of dye-surfactant aggregates (such as salts, ion pairs, molecular complexes, dye-rich induced micelles) can occur, are widely described in the literature

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[18–24]. This also applies to interactions between acridine dyes and sodium dodecyl sulfate (SDS) – a well-known detergent with a wide spectrum of applications, e.g. in washing processes [25,26] and the solubilization of protein [27,28] and organic dyes [29,30]; it can also mimic bacterial membranes [31–33].

The history of the relevant research is briefly as follows. Robinson et al. (1975) was one of the first to study the solubilization of positively charged acridine dyes by anionic micelles formed by sodium *n*-alkyl sulfates [34]. Moulik et al. (1979) described spectrophotometric, conductometric and dialysis studies of the interaction of acridine orange monohydrochloride dye with SDS [35]. Ban et al. (1983) investigated the fluorescence decay behavior of the acridine orange-sodium dodecyl sulfate system [36]. Miyoshi et al. (1988) investigated the absorption and fluorescence spectra, and the fluorescence lifetime of acridine orange over a wide range of SDS concentrations [37]. Gehlen et al. (1991) studied the fluorescence quenching of acridine orange by aromatic amines in SDS micelles [38]. Bisenbaev et al. (1993) reported on the luminescence of acridine orange in a premicellar aqueous solution of SDS [39]. Bercu et al. (1996) investigated the influence of SDS on the spectroscopic properties of proflavine and acridine yellow in aqueous media [40]. Lupan (1998) correlated the molecular properties of proflavine, acridine yellow and acridine orange in SDS micellar solution with their electronic structures [41]. Mel'nikov et al. (2001) demonstrated the influence of thallium ions on the luminescence properties of trypaflavine, acridine yellow, and acridine orange solubilized in SDS micelles [42]. Pereira and Gehlen (2005) described interactions between some acridines (acridine, 9-aminoacridine and proflavine) and SDS studied by electronic absorption, steady-state and time-resolved fluorescence spectroscopies [43]. Wiosetek-Reske and Wysocki (2006) reported on the spectroscopic and photophysical properties of *N*-nonyl acridine orange in the presence of SDS micelles [44]. Shaw and Pal (2007) investigated the fluorescence relaxation dynamics of acridine orange in SDS micelles and DNA using picosecond-resolved fluorescence spectroscopy [45]. Ganguly (2010) described the absorption and fluorescence spectra of acridine orange in solutions of different surfactants (including sodium dodecyl sulfate) [46]. Ghosh et al. (2011) studied the photophysical properties and sensory capabilities of acridine orange in the presence and absence of a biomimicking anionic SDS micellar nanocage at various pH [47]. Finally, Dutta and Dutta (2013) examined the behavior of aqueous acridine orange in the presence of submicellar anionic surfactants (including SDS) by means of UV–Vis, fluorescence spectroscopy and surface tension measurements [48].

As described above, the investigations into the interactions between acridines and sodium dodecyl sulfate were performed using a wide range of research tools, including spectroscopic, electrochemical, thermochemical and other methods. However, there is no information on studies concerning interactions between these compounds in the solid state, especially in crystals. A detailed analysis of the interactions occurring in the crystal structure of 9-aminoacridinium dodecyl sulfate may be helpful for a better understanding the self-assembled functional materials. It concerns especially those materials which contain organic dyes with conjugated π-electron systems in the context of "surface matching" [49] of the ionic layers in the crystal packing, as previously discussed in the literature [19,49–53].

In this article we describe the synthesis and structural characterization of a dye-surfactant system obtained by the reaction of 9-aminoacridine hydrochloride with sodium dodecyl sulfate, as well as the interactions occurring in the crystal structure of the title compound. Perusal of the Cambridge Structural Database search (CSD version 5.34, update August 2013) [54] shows that the crystal structure of the title compound is the first to contain the dodecyl sulfate anion and a cationic organic dye.

Experimental

Materials and synthesis

All the chemicals were purchased from Sigma Aldrich and used without any further purification. 9-Aminoacridine hydrochloride monohydrate (150 mg/0.60 mmol) (pK_a = 9.90) and sodium dodecyl sulfate (173 mg/0.60 mmol) were dissolved in 50 cm^3 water + ethanol (v/v 1:1) and boiled for *ca.* 15 min. The clear solution was allowed to evaporate for a few days to yield light-yellow single crystals of the title compound (275 mg, >99% yield; m.p. = 175.0 °C (Fig. S1); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 0.85 (t, 3H, J = 6.0 Hz, H_{1A}, SDS), 1.22 (m, 18H, H_{2A}–H_{10A}, SDS), 1.47 (m, 2H, H_{11A}, SDS), 3.68 (t, 2H, J = 6.1 Hz, H_{12A}, SDS), 7.61 (t, 2H, J = 8.0 Hz, $H_{3,6}$), 7.91 (d, 2H, J = 8.5 Hz, $H_{1,8}$), 8.05 (t, 2H, J = 7.9 Hz, $H_{2,7}$), 8.68 (d, 2H, J = 8.5 Hz, $H_{4,5}$), 9.99 (bs, 2H, NH_2), 13.64 (bs, 1H, NH) (Fig. S2a); ^{13}C{H} (NMR 125.7 MHz, DMSO-d_6) δ = 13.92 (C_{1A}, SDS), 22.06 (C_{2A}, SDS), 25.51 (C_{10A}, SDS), 28.68 (C_{9A}, SDS), 28.75 (C_{11A}, SDS), 28.99–29.06 (C_{4A}–C_{8A}, SDS), 31.26 (C_{3A}, SDS), 65.47 (C_{12A}, SDS), 111.57 ($C_{11,13}$), 118.87 ($C_{1,8}$), 123.91 ($C_{3,6}$), 124.69 ($C_{4,5}$), 135.68 ($C_{2,7}$), 139.37 ($C_{12,14}$), 157.89 (C_9) (Fig. S2b); analysis calculated/found for $C_{25}H_{36}N_2O_4S$: C 65.19/65.06, H 7.88/7.79, N 6.08/6.11, S 6.96/6.89).

X-ray crystallography

Single-crystal specimens of the title compound were selected for the X-ray diffraction experiment at T = 295(2) K (Table 1). Diffraction data were collected on an Oxford Diffraction Gemini R ULTRA Ruby CCD diffractometer with Cu $K\alpha$ (λ = 1.54184 Å) radiation. The lattice parameters were obtained by least-squares fit to the optimized setting angles of the collected reflections by means of CrysAlis CCD [55]. The structural determination was carried out using the SHELX package. The structures were solved by direct methods, with refinements being carried out by full-matrix least-squares on F^2 using the SHELXL-97 program [56]. All H-atoms bound to aromatic C-atoms were placed geometrically and refined

Table 1
Crystal data and structure refinement for title compound.

Compound	9-Aminoacridinium dodecyl sulfate
Chemical formula	$(C_{13}H_{11}N_2)^+\cdot(C_{12}H_{25}O_4S)^-$
FW/g mol^{-1}	460.63
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	20.7729(4)
b (Å)	16.6022(3)
c (Å)	7.2741(1)
α (°)	90
β (°)	97.260(2)
γ (°)	90
V (Å^3)	2488.55(7)
Z	4
T (K)	295(2)
λ_{Cu} (Å)	1.54184
ρ_{calc} (g cm^{-3})	1.229
μ (mm^{-1})	1.415
$F(000)$	992
2θ Range for data collection (°)	3.42–67.33
Completeness 2θ (%)	98.3
Reflections collected	21.477
Reflections unique	4402[R_{int} = 0.0392]
Data/restraints/parameters	4402/0/299
Goodness-of-fit on F^2	1.058
Final R_1 value ($I > 2\sigma(I)$)	0.0542
Final wR_2 value ($I > 2\sigma(I)$)	0.1479
Final R_1 value (all data)	0.0755
Final wR_2 value (all data)	0.1594
CCDC number	CCDC 986839