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Quantification of the binding preference of selected dyes at a solid–liquid interface in organized media

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Abstract: The binding behavior of anionic dyes, acid yellow 17 and acid blue 25, at an activated carbon–liquid interface has been investigated in organized media based on aqueous sodium dodecyl sulfate using differential electronic spectroscopy. The quantification of interactions occurring in the system was realized using a simple physical model, emphasizing the displacement of bound dyes from the carbon surface. The quantities of displaced dyes were comparable; however, acid blue 25 was relatively easily desorbed compared to acid yellow 17. These differences can be attributed to differences in the dye size and hydrophobicity. The model is valid for the premicellar region of the surfactant. The results throw light on some characteristics of solid–liquid interfaces.

Keywords: advance materials; dye adsorption; electronic spectral patterns; anionic surfactant.

INTRODUCTION

Many chemically and biologically significant phenomena occur at solid–liquid interfaces.[1,2] The adsorption of solute onto active carbon or a functionalized surface from solution are such processes, which are largely utilized in the treatment of industrial effluents.[3–8] Activated carbon contains condensed aromatic rings, which give rise to a sheet-like structure with voids and interstices.[9] It contains a net-work of interconnected pores, with macro and meso pores forming the adsorption surface, whereas micro pores generate the interior.[10] The forces responsible for dye localization at a solid–liquid interface include hydrogen bonding, electrostatic and van der Waals interactions.[11] In addition, a substantial contribution comes from cavitation of the solute by the microporous matrix.[10] Beside highlighting the effectiveness of an adsorption process, the alteration in spectral patterns of surface bound solute can also be harnessed for optimizing the

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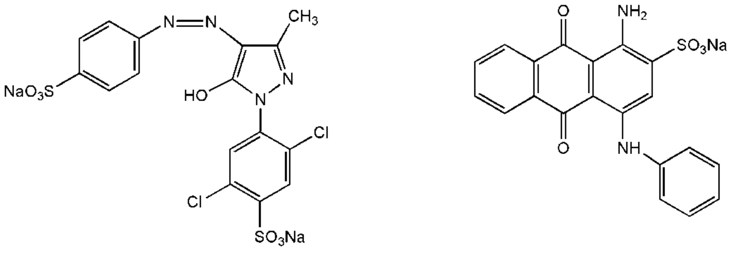
properties of advanced materials,[11,12] which may include mere surface fuctionalization by surfactants.[13]

Industrial effluents contain large proportions of surfactants[14] that can affect adsorptive removal of dyes by active carbon during waste treatment.[15] It is therefore highly imperative to systematically investigate these effects. The effect of organized media on dye interaction with certain surfaces has been extensively studied.[16–18] In addition, the competition between various solutes for localization at solid–liquid interface has been emphasized earlier.[19–21] Moreover, recently a physical model was proposed that directly related the quantities of dye bound to a solid surface with the concentration of surface active agents.[22] However, the physical model was applicable only when dye and surfactant bear opposite charges. In the present study, this limitation was overcome by adopting a different approach based on independent binding of surfactant and dye onto a solid surface. This allowed the individual association constants to be related to the displacement constant, K_{disp}, reflecting the competitive binding between the surfactant and dye. The present approach, not only allows the determination of the amount of dye at the solid–liquid interface, but also permits the computation of the quantity of surfactant entrapped onto the surface. The work was intended to cover only the pre-micellar region, so the effect of surfactant self-assembly was not emphasized.

For present study, acid yellow 17 (AY17) and acid blue 25 (AB25) were selected as dye candidates, whereas sodium dodecyl sulfate (SLS) was chosen as anionic surfactant. The molecular structures of AY17 and AB25 are provided in Fig. 1.



(a) (b)

Fig. 1. Molecular structures of: a) acid yellow 17 and b) acid blue 25.

EXPEIMENTAL

Sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$, FW 288.38, purity 99 %) was the product of Alfa Aesar. Anionic dyes acid yellow 17 ($C_{16}H_{10}Cl_2N_4Na_2O_7S_2$, FW 551.29, dye content 60 %) and acid blue 25 ($C_{20}H_{13}N_2NaO_5S$, FW 416.38, dye content 45 %) were obtained from Sigma–Aldrich. Dyes and surfactant were used without further treatment. Activated charcoal (Sigma–Aldrich) was thoroughly washed with distilled water and dried in an oven prior to use. For all preparations, ultrapure water from a Milli-Q Advantage A10 system (Millipore, France) was used.

UV–Visible absorption spectra of aqueous solutions of dyes were recorded on a Perkin Elmer Lambda 25 spectrophotometer using water as the reference. In the case of AB25, the dye was first dissolved in dimethylformamide and diluted with water to achieve the desired concentration. For one set of measurements, the quantity of charcoal was fixed, whereas the surfactant concentration was varied from 0.8 to 8.0 mM. The concentration of dye in the solution was 0.01 g L^{-1}. The conical flasks were stoppered to avoid loses during adsorption, the contact time was 90 min, the flasks (each of 50 mL volume) contained pre-weighed adsorbent and were shaken at 200 rpm using an orbital shaker (Thermo Scientific), the *S*/*L* ratio was maintained at 40 g L^{-1}. The charcoal was removed by filtration or centrifugation from the equilibrated mixtures. A circulating water thermostat was used to maintain the temperature within ±0.1 °C. The absorbance values at maximum wavelength were employed. Under these experimental conditions, the dyes predominantly existed in the monomeric form.[23]

The specific conductance of the surfactant solutions were determined using a microprocessor conductivity meter (WTW), LF 2000/C, Germany. During an experimental run, the temperature was maintained at 25.0±0.1 °C. The critical micelle concentration of aqueous SLS obtained from a plot of specific conductance *vs*. surfactant concentration was 8.2 mM. The pH of each solution was recorded at room temperature using an Orion Star A111 pH bench-top meter from Thermo Scientific. Although the individual dyes exhibited pH 6.2 (AY17) and 6.4 (AB25), only slight variation in pH was observed during the adsorption experiments.

Molinspiration® was used for computation of log *P* values, topological polar surface area and volume of each dye molecule.

Theoretical approach

In a system based on surfactant, dye and adsorbent, the adsorbent surface can accommodate both surfactant and dye and binding of either of the adsorbates is assumed to occur independently, provided the solutes exist in low amounts in solution.

The occupancy of binding site C by a surfactant monomer S onto the surface of an adsorbent, can be depicted by the following equilibrium:

$$\mathrm{S + C \leftrightarrows SC}$$

which can be represented by equilibrium constant K_{SC}:

$$K_{\mathrm{SC}} = \frac{a_{\mathrm{SC}}}{a_{\mathrm{S}} a_{\mathrm{C}}} \tag{1}$$

where, a_{S}, a_{C} and a_{SC} are the activities of surfactant, adsorbent (reflecting total number of binding sites) and bound surfactant, respectively.

Similarly, the dye occupancy of a binding site C can be represented by the expression:

$$\mathrm{D + C \leftrightarrows DC}$$

The equilibrium constant K_{DC} for this expression will be:

$$K_{\mathrm{DC}} = \frac{a_{\mathrm{DC}}}{a_{\mathrm{D}} a_{\mathrm{C}}} \tag{2}$$

where a_{D}, a_{C} and a_{DC} represent the activities of dye, charcoal and entrapped dye, respectively.

The probability of the displacement of bound dye by surfactant is increased with increasing surfactant concentration, especially when dye and surfactant bear the same charges and cannot engage in ion-pair formation. In this case, the displacement equilibrium expression will be:

$$\mathrm{DC + S \leftrightarrows SC + D}$$

and represented by a displacement constant K_{disp} as:

$$K_{\mathrm{disp}} = \frac{a_{\mathrm{SC}} a_{\mathrm{D}}}{a_{\mathrm{DC}} a_{\mathrm{S}}} \tag{3}$$

where a_{D}, a_{S} are the activities of free dye and surfactant, whereas a_{SC} and a_{DC} are those of bound dyes and surfactant, respectively.

In fact, the displacement constant is reflective of all the associations taking place in systems. It is apparent that:

$$K_{\mathrm{disp}} = \frac{K_{\mathrm{SC}}}{K_{\mathrm{DC}}} \tag{4}$$

Considering the dilute solutions, such that activity coefficients approach unity,[24–26] Eqs. (1)–(3) can be transformed to the corresponding Eqs. (5)–(7):

$$\frac{q_{\mathrm{SC}}}{q_{\mathrm{C}}} = N_{\mathrm{o}} K_{\mathrm{SC}} + N_{\mathrm{SC}} K_{\mathrm{SC}} \tag{5}$$

$$\frac{q_{\mathrm{DC}}}{q_{\mathrm{C}}} = D_{\mathrm{o}} K_{\mathrm{DC}} + N_{\mathrm{DC}} K_{\mathrm{DC}} \tag{6}$$

and

$$\frac{N_{\mathrm{D}}}{q_{\mathrm{DC}}} = \left(\frac{N_{\mathrm{o}}}{q_{\mathrm{SC}}}\right) K_{\mathrm{disp}} + \frac{K_{\mathrm{disp}}}{M_{\mathrm{s}}} \tag{7}$$

where N_{o} and D_{o} are the total concentrations of surfactant and dye, respectively. N_{SC} and N_{DC} are the concentrations of charcoal-bound surfactant and dye, respectively, and their corresponding quantities adsorbed onto charcoal are q_{SC} and q_{DC}. q_{C} is the quantity of adsorbent. N_{D} is the equilibrium dye concentration and M_{s} is the molar mass of the surfactant.

RESULTS AND DISCUSSION

Each dye candidate showed two peaks in their UV–Vis spectrum in the presence of aqueous sodium dodecyl sulfate. The λ_{max} values obtained for AY17 and AB25 were 419 and 600 nm, respectively. These values were slightly blue shifted compared to those reported in the literature[23,27] and reflected the effect of the surfactant. The corresponding molar extinction coefficients were 2.28×10^4 and 4.15×10^3 L mol^{-1} cm^{-1}, respectively.

The physical model was applied to each dye and the relationship between $N_{\mathrm{D}}/q_{\mathrm{DC}}$ and surfactant concentration, N_{o}, for AY17 is shown in Fig. 2. The corresponding values of the differential absorbance utilized to determine the quantity of bound dye are gathered in Table I.

The ΔA values were measured at the λ_{max} of AY17. A continuous decline in quantity of surface bound dye was observed with increasing surfactant concentration. This reflects the competitive binding between surfactant and dye at a solid–liquid interface.[22] AY17 bears sulfonate groups, which do not favorably bind to electron-rich functionalities on the charcoal surface, which are likely to exist at pH of 6.6–7.2 recorded during the present work. In contrast, SLS can attach to charcoal through hydrophobic interactions.[28] Therefore, the dye displacement is facilitated.

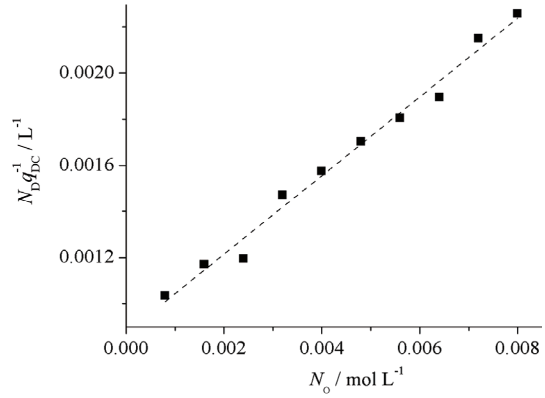


Fig. 2. Relationship between N_D/q_{DC} and SLS concentration for AY17.

TABLE I. Differential absorbance (ΔA) and quantity of adsorbed dye (q_{DC}) as a function of surfactant concentration (N_o)

N_o / mol L^{-1}	AY17		AB25	
	ΔA	q_{DC} / mg	ΔA	q_{DC} / mg
0.0008	0.263	6.33	0.060	6.03
0.0016	0.251	6.04	0.058	5.88
0.0024	0.249	6.00	0.053	5.34
0.0032	0.228	5.49	0.050	5.03
0.0040	0.221	5.32	0.049	4.94
0.0048	0.213	5.13	0.044	4.49
0.0056	0.207	4.98	0.039	3.94
0.0064	0.202	4.86	0.038	3.81
0.0072	0.189	4.55	0.037	3.75
0.0080	0.184	4.43	0.038	3.83

To investigate the system further, another dye acid blue 25 was utilized. AB25 possesses only one sulfonate group. It is also more hydrophobic compared to AY17. This dye exhibited trends similar to those observed with AY17 and the quantity of surface bound dye was reduced upon surfactant addition (Fig. 3). The corresponding ΔA values measured at the λ_{max} of AB25 and the quantity of adsorbed dye are provided in Table I. A pH variation over a narrow range of 6.7–7.0 occurred during the experiment.

Two differences were apparent regarding the binding behavior of dye candidates. First, a greater quantity of AY17 existed at the surface compared to AB25 at any stage up to the N_o value of 7.2 mM.

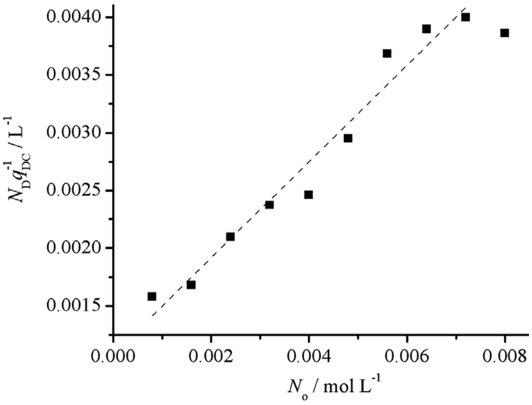


Fig. 3. Relationship between N_D/q_{DC} and SLS concentration for AB25.

This indicates that at slightly acidic or neutral pH values encountered during the investigation, a notable proportion of undissociated oxygen-containing functionalities (such as –COOH and –OH) exist on the surface active carbon that allow the bonding of the dye's sulfonate groups to the solid surface *via* hydrogen bridges. Second, the entrapment of AB25 was promoted, whereas that of AY17 was inhibited when the N_o value was 8.0 mM, probably because of the hydrophobicity of AB25 and also due to its ability to engage in hydrogen bonding interactions (Fig. 4).

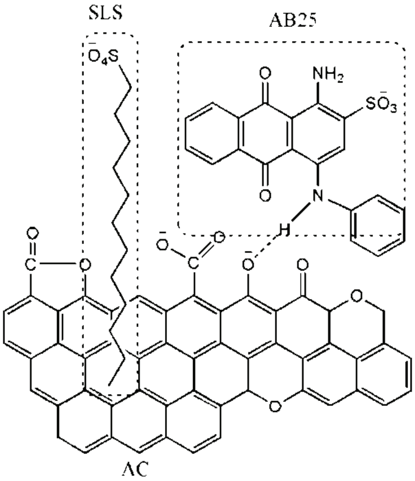


Fig. 4. Binding modes of SLS and AB25 onto the surface of activated charcoal.

The displacement constants K_{disp} obtained from Eq. (7) (Figs. 2 and 3) are given in Table II. The low magnitudes of K_{disp} reveal that significant proportions of the dyes exist at the solid–liquid interface and only small amounts of the dyes are replaced by surfactant.

TABLE II. Displacement constant (K_{disp}) and concentration of adsorbed surfactant (N_{SC}) for the ternary systems

Dye	$K_{\mathrm{disp}}\times10^{-2}$	$N_{\mathrm{SC}}\times10^{-3}$ / mol L^{-1}
AY17	25.18	2.66
AB25	31.14	1.79

The maximum quantities displaced Δq_{DC} by SLS were 1.90 and 2.28 mg for AY17 and AB25, respectively. Although the difference is not large, the values indicate that AB25 is replaced comparatively easier by SLS than AY17. AB25 can also attach to the surfactant head groups through hydrogen bonding, which is expected to promote its displacement from the interfacial area. The log P values computed for AY17 and AB25 were –0.71 and 0.9, respectively, indicating the greater affinity of AY17 for the aqueous phase. The topological polar surface areas exhibited by these dyes were 171.80 and 129.39 Å^2 for AY17 and AB25, respectively. Based on these values, a smaller adsorption of AY17 compared to AB25 could be expected, especially when surfactant adsorption (with SO_4^- groups directed almost perpendicular to solid surface) also enhances the number of negative charges on the carbon surface in the pH range observed during the study (Fig. 4). It appears that cavitation of dyes into voids on adsorbent surface also plays a role. The volume occupied by single molecule of AB25 is 314.38 Å^3 whereas that of AY17 is 352.6 Å^3. Hence, the two dyes differ approximately by a factor of 3 Å in size. Smaller dyes are trapped by larger pores but are not retained.[9] On the other hand, the micro pores may not be accessible to solute molecules above a certain size. This could be the reason for greater displacement of AB25 by SLS, compared to AY17. The adoption of different binding modes by AY17 and AB17 is indicated in Figs. 2 and 3, where AY17 shows nearly a linear trend, while discrete regions of different slopes can be identified for AB25. The concentration of charcoal-bound surfactant is smaller in the presence of AB25 than in the AY17-based system, which leads to the conclusion that AB25 desorption is partly due to lack of its retention within the pores on the surface of the adsorbent. The log P value for SLS is 1.78, its topological polar surface area is 66.43 Å^2 and the volume occupied by a single SLS molecule is 259.71 Å^3. Hence, surfactant molecules may lay flat at the solid surface,[9] forming a monolayer at the solid–liquid interface with their polar head-group directed towards the water and hydrophobic tail interacting with the carbon surface or simply aligned at the air–solution interface with the anionic sulfate group immersed in solution, and the tail pointing to the air. Irrespective of the number of dye molecules displaced, the competing process of formation of monolayer at the air–solution interface will also reduce the amount of SLS existing at solid–liquid interface. Similar effects on dye adsorption have been related to dye content, where the presence of impurities masks the differential adsorption.[29]

CONCLUSIONS

The binding behavior of anionic dyes AY17 and AB25 onto surface of activated charcoal in organized media reflects the selectivity of activated carbon––liquid interface for dye residence. SLS competes with the dyes for surface attachment, but the efficiency of displacement is low. This is probably due to presence of electrostatic repulsive interactions between anionic sulfonate group and electron rich functionalities existing on the surface of activated carbon. The competitive adsorption of dyes was quantified in terms of the displacement constant by employing a simple model. The magnitudes of parameters, such as $K_{\rm disp}$ revealed that AB25 was desorbed by surfactant comparatively easier than AY17. The binding behavior of dyes was reflective of their sizes and hydrophobicity. The proposed model was found valid for the pre-micellar region of the anionic surfactant. These findings have significance for the development of functionalized materials,[1,30] especially those involving low amounts of surface-active agents.[31]

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ИЗВОД

КВАНТИФИКАЦИЈА ПРЕФЕРЕНЦИЈАЛНОГ ВЕЗИВАЊА ОДАБРАНИХ БОЈА НА МЕЂУПОВРШИНИ ЧВРСТО–ТЕЧНО У ОРГАНИЗОВАНОМ МЕДИЈУМУ

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Понашање при формирању веза анјонских боја, acid yellow 17 и acid blue 25, на међуповришини активни угаљ–течност је испитивана у организованом медијуму базираном на течном натријум-лаурилсулфату коришћењем диференцијалне UV спектроскопије. Кванитификација интеракција које се дешавају у систему је урађена применом једноставног физичког модела, са акцентом на истискивање везаних боја са површине угљеника. Количине истиснутих боја су упоредиве, с тим што се acid blue 25 једноставније десорбује у поређењу са acid yellow 17. Ове разлике се могу приписати разлици у величини боје и хидрофобности. Модел важи за пре-мицеларни опсег сурфактанта. Резултати објашњавају неке карактеристике међупровршине чврсто–течно.

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