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Solubilization of Water-Insoluble Dyes by Polyion/Surfactant Complexes

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Solubilization data for the water-insoluble dyes *o*-(2-amino-1-naphthylazo)toluene (OY) and 1-pyrenecarbaldehyde (PyA) in mixed solutions of anionic polyelectrolyte and a cationic surfactant are reported. The polymers used were sodium dextran sulfate (DxS) and the sodium salt of poly(styrenesulfonic acid) (PSS). The surfactants used were dodecyltrimethylammonium bromide (DTAB) and tetradecyltrimethylammonium bromide (TTAB). DxS exhibited a highly cooperative binding of the surfactant ions, while binding to PSS occured at lower surfactant concentrations, but was less cooperative. DxS/surfactant complexes had a larger solubilization capacity per bound surfactant ion for both OY and PyA than did PSS/surfactant complexes. The standard Gibbs energy changes for solubilization in DxS/DTAB were determined to be 4.0 kJ mol^{-1} for OY and 5.4 kJ mol^{-1} for PyA; the values in PSS/DTAB were 6.5 kJ mol^{-1} for OY and 9.3 kJ mol^{-1} for PyA. The solubilization capacities and standard Gibbs energy changes of polyion/surfactant complexes strongly relate to the binding mode of the surfactant. The differences in the solubilization capacities and standard Gibbs energy changes between polyion/surfactant complexes and DTAB or TTAB micelles, and between OY and PyA, are discussed in relation to the aggregate size and solubilizate location.

Aqueous systems containing both polymers and surfactants are encountered in such diverse applications as tertiary oil recovery, drug delivery, paint formulation, and pulp and paper production.[1] This varied use of polymer–surfactant systems is partly based on the formation of hydrophobic domains in polymer–surfactant complexes in aqueous solutions, leading to the observed solubilization properties of polymer–surfactant systems for water-insoluble materials.[2—15] Although solubilization in micellar systems has been extensively studied in order to understand the molecular mechanism of this process,[12,16—29] only a limited number of papers have been published concerning the solubilization mechanism in polymer–surfactant systems. In an earlier paper we reported on a study concerning the solubilization of an oil-soluble dye, *o*-(2-amino-1-naphthylazo)toluene (OY), by the poly(vinyl sulfate) (PVS)–dodecyltrimethylammonium complex, and proposed a concerted cooperative binding mechanism for this process.[13] According to this mechanism, the solubilization capacity is related to the cooperativity of the binding process of the surfactant to the polymer; this cooperativity, in turn, is related to the aggregate size in the mixed system. In previous studies we reported on differences in cooperativity in the binding of cationic surfactants to the anionic polyelectrolytes dextran sulfate (DxS) and poly(styrenesulfonate) (PSS).[30,31]

In the present paper we compare the solubilization of OY and 1-pyrenecarbaldehyde (PyA) in DxS and PSS–surfactant complexes using cationic surfactants of varying alkyl chain length (Chart 1). The results show large changes in the solubilization capacity, depending on the degree of cooperativity of the surfactant binding process by the polyelectrolyte.

Experimental

Materials. The sodium salts of dextran sulfate (Wako, Osaka) and poly(styrenesulfonate) (Polysciences, Warrington, PA) were purified as described before.[30] The concentration of ionic groups was determined by colloid titration with standard solutions of 0.0025 monomer mol dm^{-3} poly(diallyldimethylammonium chloride) (Wako, Osaka) and 0.0025 monomer mol dm^{-3} potassium poly(vinyl sulfate) (Wako, Osaka), and toluidine blue indicator

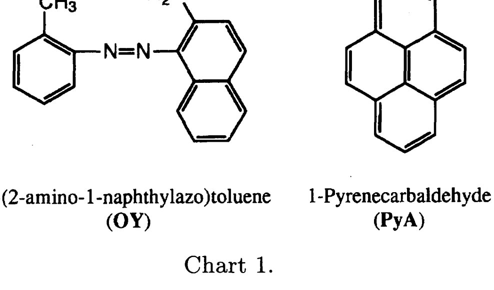

Chart 1.

(Wako, Osaka). The polyion concentration is represented by the ionic group basis. Dodecyltrimethylammonium bromide (DTAB) and tetradecyltrimethylammonium bromide (TTAB) (GR, TCI, Tokyo) were purified by repeated recrystallization from ethanol. The water-insoluble dyes, *o*-(2-amino-1-naphthylazo)toluene (OY, Tokyo Kasei) and 1-pyrenecarbaldehyde (PyA, Aldrich), were used without further purification. NaCl (GR) was commercially obtained and used without further purification. The water used was doubly distilled.

Measurements. A few milligrams of OY or PyA powder were added to 20 mL mixed solutions of 0.5 mmol dm^{-3} polyelectrolyte, sodium chloride, and surfactant at the required concentration; the mixture was shaken at 25 °C for 3 d. Sodium chloride was added so as to keep the solution ionic strength constant and to depress too strong binding of DTA$^+$ by PSS in order to measure the equilibrium concentration of the DTA$^+$ ion. The supernatant was collected for absorption measurements and potentiometry after standing for an additional day at 25 °C. The amount of free (non-bound) surfactant was determined potentiometrically using an electrode responsive to the cationic surfactant ion used; the amount of surfactant bound to the polyion was calculated.[32] The amount of OY solubilized in the polyion/surfactant mixture was calculated from the molar absorbance of the OY in the mixture (OY is completely insoluble in the absence of a polyion or a surfactant). The molar absorbance used for OY was the value in ethanol (determined to be 13300 mol^{-1} dm^3 cm^{-1}), because the absorption spectrum in ethanol is very similar in shape to that in the polyion/surfactant solution. For PyA the molar absorbance at 397 nm in a micellar solution of TTAB, determined to be 4350 mol^{-1} dm^3 cm^{-1}, was used.

Results and Discussion

Surfactant Binding by DxS and the Cooperative Binding Model. Examples of emf measurements using the surfactant ion-selective electrode are given for DTAB in Fig. 1, where the solid symbols are for the calibration curve in the absence of polyion and the open symbols are for the polyion-surfactant mixture. The calibration curves exhibit a linear relationship down to 10^{-5} mol dm^{-3} DTAB with nearly a Nernstian slope (typically slopes of 57.9—59.6 mV are found). In the presence of polyelectrolyte, the deviation to lower emf values indicates the lower free surfactant ion concentration due to binding to the polyion. A comparison of the measured emf values in the presence of polyion to the calibration curve allows us to calculate the equilibrium concentration of the free surfactant, and, thereby, the amount of bound surfactant.

Surfactant binding isotherms, represented as plots of the degree of binding, (β; defined as the mole ratio of bound surfactant ions to the number of ionic groups on the polyion) vs. the equilibrium concentration of the free surfactant, ($[\mathrm{S}]_\mathrm{f}$) are given in Fig. 2A for DxS/DTAB and in Fig. 2B for PSS/DTAB. The open and solid symbols represent the values for the absence and presence of OY, respectively.

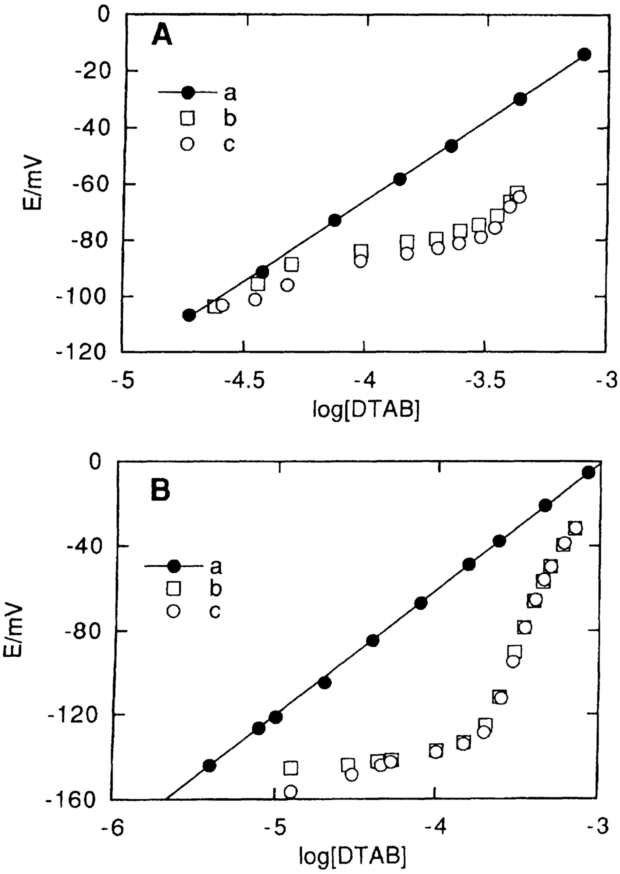

Fig. 1. Electromotive force by DTA$^+$ ion in the absence (a) and presence (b, c) of DxS (A) and PSS (B). a. DTAB only, b. without OY, c. with OY.

If we first concentrate on the data in the absence of a dye (open symbols), the isotherms in Fig. 2A show a steep rise in the amount of bound surfactant at a critical free-surfactant concentration. This indicates a highly cooperative binding process of DTAB by DxS, induced by hydrophobic interactions between bound surfactant ions.[30] In previous studies we successfully analyzed these binding isotherms with a linear lattice model which included only nearest-neighbor interactions.[33,34] In this cooperative binding model two parameters are introduced: K is the binding constant for a surfactant ion to an isolated site on the polyion (Eq. 1), and Ku is the binding constant for a site next to a site already occupied by a surfactant ion (Eq. 2):

$$(\mathrm{OO}) + \mathrm{S} \xrightleftharpoons{K} (\mathrm{OS}), \tag{1}$$

$$(\mathrm{SO}) + \mathrm{S} \xrightleftharpoons{Ku} (\mathrm{SS}). \tag{2}$$

In this notation (O) stands for an empty binding site on the polyion, and (S) for a site occupied by a surfactant ion. This model leads to the following equation for the degree of surfactant binding, (β):[33,34]

$$\beta = \frac{1}{2}\left\{1 + \frac{s-1}{[(s-1)^2 + 4s/u]^{1/2}}\right\}. \tag{3}$$

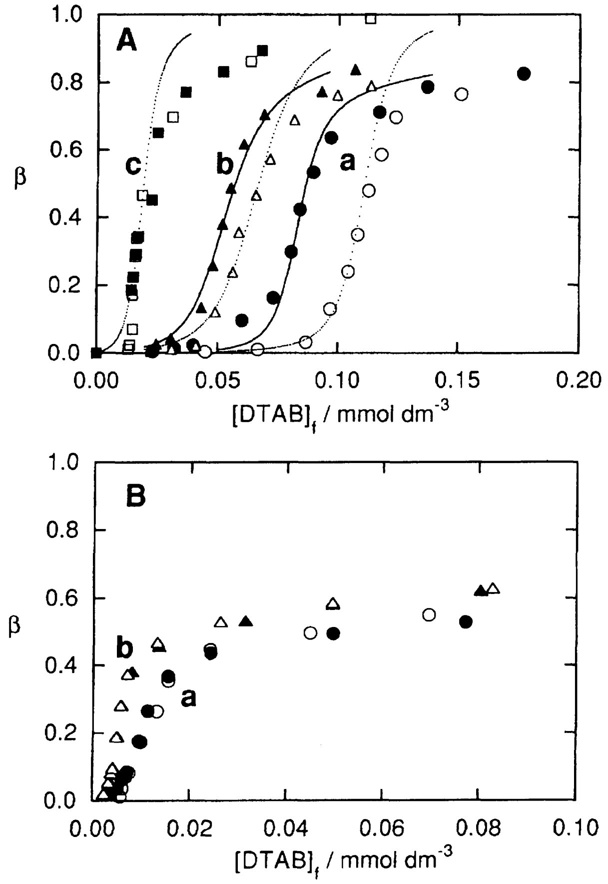

Fig. 2. Binding isotherms of DTA$^+$ ions by DxS (A) and PSS (B) at various concentration of NaCl. a. 40, b. 20, c. 5 mmol dm^{-3}. Solid marks for the data in the presence of OY and open marks for the data in the absence of OY.

Here $s=Ku$ $[\mathrm{S}]_\mathrm{f}$. The parameter u measures the cooperativity of surfactant binding: $u=1$ for non-cooperative or Langmuir type binding, and $u>1$ for a cooperative binding mode. The solid curves in Fig. 2A were calculated from Eq. 3 using the K and u values listed in Table 1. Note that Ku decreases with increasing NaCl concentration due to a weakened electrostatic attraction between the polyion and surfactant ion in solutions of high ionic strength; on the other hand, u increases with increasing NaCl concentration.

Figure 2A indicates that the presence of OY shifts the DTA$^+$ binding isotherms (solid symbols) to lower DTAB equilibrium concentrations for the isotherms at 20 and 40 mmol dm^{-3} NaCl. This observation indicates that the DxS/DTAB complex solubilizes OY, and that the presence of solubilized OY promotes a further binding of DTAB. In a previous paper we called this a concerted cooperative binding process, and proposed a binding model in which OY is assumed to be bound to a site next to a site already occupied by a surfactant ion.[13] This concerted cooperative binding model can be represented by the following equilibrium:

$$(\mathrm{SOS})+\mathrm{D}\xrightleftharpoons{Kd}(\mathrm{SDS}), \tag{4}$$

where again (O) is an unoccupied site, neighbored by two surfactant occupied sites (S). (D) is a site occupied by the dye, i.e. OY in our case. Note that a dye molecule binds to a site surrounded by bound surfactants. This model leads to the following equation for the degree of surfactant binding, (β):

$$\beta=\frac{s}{2(s+d-s/u)}\left\{1-\frac{1}{\mathrm{u}}+\frac{s+d-1+(1+d-s)/u}{[(s+d-1)^2+4s/u]^{1/2}}\right\}. \tag{5}$$

In this equation d equals Kd $[\mathrm{OY}]_\mathrm{f}$. In the present system d is constant because the OY solution is always saturated (i.e. $[\mathrm{OY}]_\mathrm{f}$ is constant). The parameter d measures the free energy gain for dye solubilization and the enhancement of surfactant binding through the increased hydrophobic interaction.

Using the K and Ku values obtained from the best fit of Eq. 3 to the binding data in the absence of OY, we can now use Eq. 5 to calculate the binding isotherms in the presence of OY, varying the value of d (and therefore Kd) to obtain the best fit to the experimental binding isotherms. The best-fit values of d are also given in Table 1; the curves with these values for K, u, and d are given as solid curves in Fig. 2A. The parameter d predicts a shift of the binding isotherms to a lower concentration of free surfactant, indicating an enhancement of surfactant binding. The binding curves in 5 mmol dm^{-3} NaCl with and without a dye present are identical; therefore, for this case the model would predict that $d=0$, even though the absorbance data clearly indicate that OY is solubilized in this system. The value of d that we obtained increases with increasing NaCl concentration. This behavior in DxS/DTAB is opposite to the previous results for OY solubilization in poly(vinyl sulfate)/cationic surfactant systems, where d was found to decrease with increasing NaCl concentration.[13]

Table 1. Binding Parameters for Surfactant Binding by Polyion

[NaCl]/mM	Ku	u	Ku	u	d
	DTAB/DxS		OY/DTAB/DxS		
5	52	30	52	30	0
20	15	50	15	50	0.2
40	9	350	9	350	0.25
	DTAB/PSS		OY/DTAB/PSS		
20	54	9	54	9	0
40	120	10	120	10	0

Surfactant Binding by PSS. The binding isotherms in the PSS/DTAB mixed systems (Fig. 2B) are very different from the DxS/DTAB case. In PSS/DTAB, binding of DTA$^+$ ions starts at a lower concentration, suggesting a stronger interaction between DTA$^+$ and PSS compared to DxS. However, the isotherms quickly saturate at a binding degree of about

0.5, followed by a very slow increase of β. The presence of OY causes only minor changes in the surfactant binding. The K and u parameters reported in Table 1 are calculated by fitting Eq. 3 to the data for only β values lower than 0.4. The lower value of u and higher value of Ku in the PSS system at the same NaCl concentration are in agreement with our earlier results.[30,31] According to the linear cooperative binding model the lower value of u indicates a lower degree of aggregation and smaller aggregate sizes in the PSS/DTAB system compared to DxS/DTAB.

Solubilization of OY. OY is insoluble in both water and DxS solution, and also in a surfactant solution below the critical micelle concentration (cmc: 16 mmol dm^{-3} for DTAB). Figure 3A shows no absorbance at 450 nm by OY in the presence of 0.39 mmol dm^{-3} DxS without a surfactant. The addition of DTAB induces solubilization of OY only when the critical polyion-surfactant aggregation concentration of the DxS/DTAB system is exceeded. At a high DTAB concentration, phase separation leads to the presence of a faint turbidity or red precipitation, resulting in the observed absorption decrease in solutions with 5 and 20 mmol dm^{-3} NaCl. Complete phase separation was observed in a 40 mmol dm^{-3} NaCl solution for DTAB concentrations above 0.35 mmol dm^{-3}; in that case no OY was left in the supernatant. In the PSS/DTAB mixed system (Fig. 3B), although the OY absorbance increased with increasing DTAB concentration, a very small absorbance of OY was observed, even in the absence of DTAB, indicating a weak solubilization capacity of the PSS solution not found for DxS. On the other hand, although the rate of absorbance increase with increasing DTAB concentration was less in PSS/DTAB mixtures than in DxS/DTAB solutions, the increase in binding started at a lower DTAB concentration in PSS relative to DxS. Although these observations clearly demonstrate the solubilization of OY by both polyion/DTAB complexes, they also point at differences due to the different properties of the polyion/surfactant complexes in these two systems. The differences in the solubilization mechanism between DxS and PSS are closely associated with the different binding properties of DTA$^+$ ions by the polyions. The less cooperative binding system of PSS/DTAB forms small surfactant clusters, leading to a smaller solubilization capacity, while the highly cooperative binding system of DxS/DTAB induces relatively large surfactant clusters, leading to a large solubilization capacity.

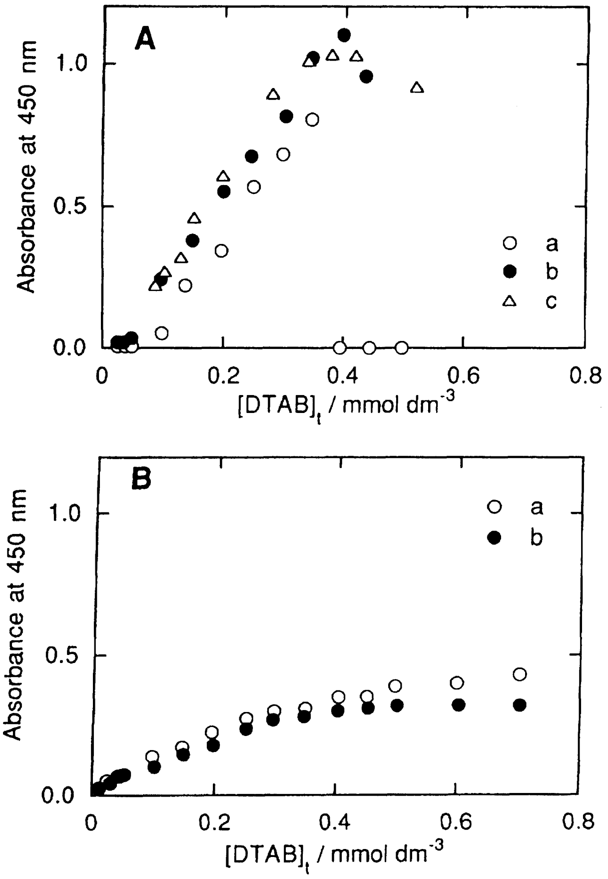

Fig. 3. Dependence of absorbance by OY on surfactant concentration in the presence of DxS (A) and PSS (B) at various [NaCl] concentrations. a. 40, b. 20, c. 5 mmol dm^{-3} NaCl.

Thermodynamics of Solubilization. We define the solubilizing capacity (P_S) as the ratio of the amount of solubilized OY to the amount of bound surfactant, $P_S = \beta_D/\beta$; β_D is the ratio of solubilized dye molecules to polyion sites. Thus, P_S represents the number of solubilized dye molecules per bound surfactant ion. Figure 4 shows that for OY solubilization the observed values of β_D vary linearly with the degree of surfactant binding, (β). We note that for a given degree of surfactant binding the dye solubilization is virtually independent of the NaCl concentration. We also note that in a 40 mM NaCl solution (1 M = 1 mol dm^{-3}) phase separation occurs at a higher DTAB concentration, leading to a colorless bulk supernatant solution. No data are

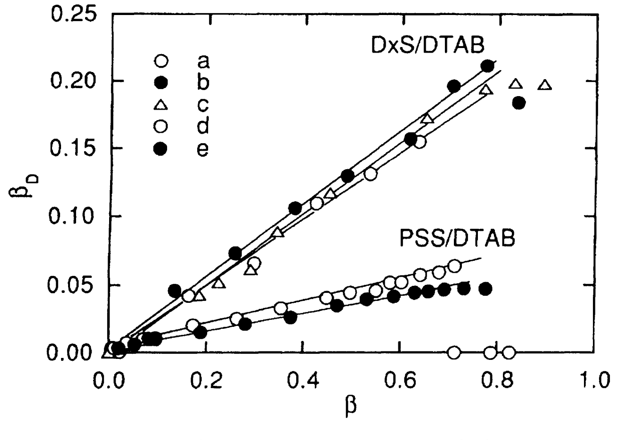

Fig. 4. Plots of solubilized amount of OY versus bound amount of DTA$^+$ ions to DxS and PSS. a. 40, b. 20, c. 5, d. 40, e. 20 mmol dm^{-3} NaCl.

given in this region. The tendency towards saturation observed at high β values for some of the curves in Fig. 4 is attributed to the onset of phase separation, as manifested by a faint turbidity. The solubilizing capacity (P_S) can be calculated from the slopes of the linear part of the data sets in Fig. 4; the values are listed in Table 2. This table includes the P_S values for micellar DTAB without polyelectrolyte. It is clear from Fig. 4 and Table 2 that the DxS/DTAB system has a higher solubilization capacity for OY than both PSS/DTAB and DTAB micelles. DxS/DTAB complexes on average solubilize about 1 OY molecule for every 4 bound DTA$^+$ ions, whereas the PSS/DTAB complexes can only solubilize 1 OY molecule for every 12 bound DTA$^+$ ions, a value comparable to the capacity of DTAB micelles.

From the solubilizing capacity we can estimate the solubilization constant (K_S) and the standard Gibbs energy change, (ΔG°), for solubilization of the dye. When we represent the solubilization equilibrium by

$$\mathrm{D(solid)} \overset{K_S}{\rightleftarrows} \mathrm{D(in\ P/S\ complex)} \qquad (6)$$

the following equation for the solubilization constant K_S is derived:

$$K_S = \frac{P_S}{1+P_S} = \exp\left(-\frac{\Delta G^\circ}{RT}\right). \qquad (7)$$

Here, ΔG° corresponds to the standard Gibbs energy of transfer of the dye from the solid phase (or saturated solution) to a polyion/surfactant complex. The values of K_S and ΔG° for OY solubilization are also presented in Table 2. The K_S values in the DxS/DTAB mixed system are three-times larger than in the PSS/DTAB mixed system, and K_S is independent of the added NaCl concentration. This finding may in part be ascribed to the formation of larger surfactant aggregates in the DxS/DTAB mixed system, related to the higher degree of cooperativity observed in the binding isotherms. Another highly cooperative binding system studied earlier, PVS/DTAB, also shows large K_S values for OY binding.[13]

Table 2. Thermodynamic Parameters for Solubilization of OY

Medium	[NaCl] / mmol dm^{-3}	P_S	K_S	ΔG° / kJ mol^{-1}
DxS/DTAB	5	0.25	0.20	4.0
	20	0.27	0.21	3.8
	40	0.25	0.20	4.0
PSS/DTAB	20	0.076	0.071	6.6
	40	0.082	0.076	6.4
PVS/DTAB[a]	20	0.47	0.32	2.8
DTAB Micelle	40	0.089	0.082	6.2

a) Ref. 13.

Table 3. Thermodynamic Parameters for Solubilization of PyA in the Presence of 40 mM NaCl

Medium	Surfactant	P_S	K_S	ΔG°/kJ mol^{-1}
DxS/Surfactant	DTAB	0.13	0.11	5.4
	TTAB	0.14	0.12	5.2
PSS/Surfactant	DTAB	0.025	0.024	9.3
	TTAB	0.018	0.018	9.9
Micelle	DTAB	0.11	0.099	5.7
	TTAB	0.19	0.16	4.5

Finally, Table 3 shows the solubilization parameters (P_S, K_S, and ΔG°) for the second dye, 1-pyrenecarbaldehyde (PyA), as calculated from the slope of the linear plots in Fig. 5. For this dye experiments were also performed with TTAB as a cationic surfactant. For PyA the solubilization capacity is independent of the surfactant chain length, similar to our observation for OY in PVS/cationic surfactant complexes.[13] Although it is generally observed that the cooperativity of the surfactant binding process is higher for surfactants with higher chain lengths,[35] we find here that K_S for the solubilization of PyA in the polymer-surfactant complexes does not depend on the surfactant chain length. For PyA we also find that the values of P_S and K_S are much higher for the DxS/surfactant mixed systems than for the PSS/surfactant mixed systems. The solubilization capacity for PyA is lower than that for OY. On the other hand, in micellar systems the DTAB and TTAB micelles solubilize more PyA than OY, and in the micellar systems the P_S and K_S values are higher for TTAB than for DTAB. This difference in solubilization capacity for OY and PyA may be related to the location of the solubilizates. We expect that although PyA and other aromatic solubilizates to be located in the palisade region of the cationic micelles,[36,37] in the polymer-surfactant complexes the ionic groups of the

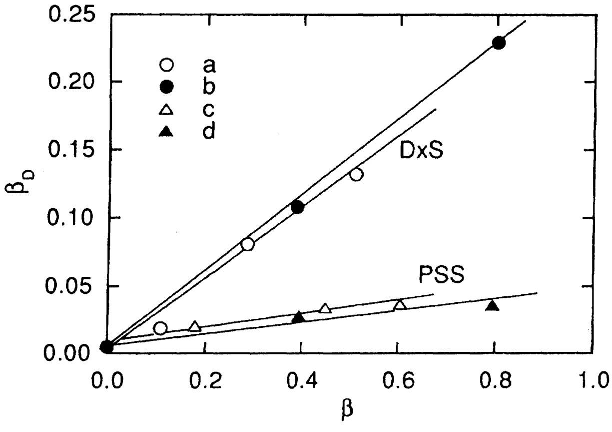

Fig. 5. Plots of solubilized amount of PyA versus bound amount of DTA$^+$ and TTA$^+$ ions to DxS and PSS. a. DTAB/DxS, b. TTAB/DxS, c. DTAB/PSS, d. TTAB/PSS.

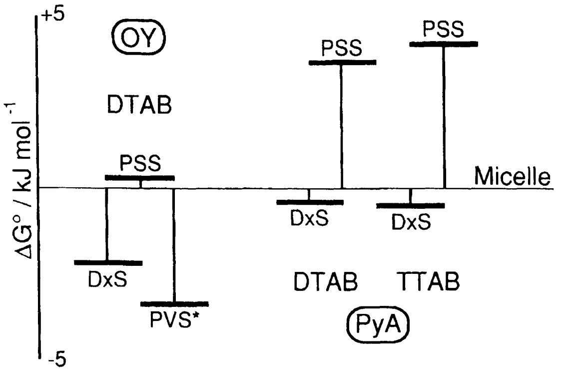

Fig. 6. Comparison of standard Gibbs energy changes for the solubilization of OY and PyA in polymer-surfactant complexes relative to solubilization in surfactant micelles.

surfactant reside on the polyion charge, and the space available for PyA may only be small. On the other hand, OY may reside closer to the polyion charge, competing with the surfactant headgroup.

Figure 6 compares the standard Gibbs energy changes for the solubilization of OY and PyA in the polyion/surfactant complexes studied to those in DTAB and TTAB micelles. Our general finding is that polyion–surfactant complexes solubilize both OY and PyA, but to a different extent, depending on the nature of the complexes and the solubilizates. Polyion–surfactant complexes with high cooperativity of the surfactant binding process, such as PVS/DTAB and DxS/DTAB, have a higher dye complexation capacity than, for instance, PSS/DTAB, a system which also exhibits a lower surfactant binding cooperativity. This observation suggests that the solubilization capacity is related to the aggregate size of the polymer–surfactant complex. The striking difference in the solubilization behavior between OY and PyA in polymer/surfactant and micellar systems may be related to the different locations of the OY and PyA dyes in the micelles, as opposed to the polymer-surfactant complexes. In general, our data have shown that the oil-soluble dye OY is effectively solubilized in complexes of anionic polyelectrolytes and cationic surfactants with high cooperativity of the surfactant binding process. The solubilization capacity of these complexes for OY is higher than the solubilization capacity of the surfactant micelles in the absence of a polymer, when expressed based on the maximum dye molecule to the surfactant molecule ratio.

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