Surface Potentials of Hydrophobic Microdomains in Aqueous Solutions of Poly(dimethyldiallylammonium-*co*-methyl-*n*-dodecyldiallylammonium salts) with Different Counterions. Evidence for the Existence of a Critical Aggregation Concentration

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The solvatochromic acid-base indicator 1-hexadecyl-4-[(oxocyclohexadienylidene)ethylene]-1,4-dihydropyridine (HOED) was used to determine surface potentials (Ψ) of micelles formed from methyldiallyl-*n*-dodecylammonium salts containing different counterions (MDDAX, X = Cl, Br, I, benzoate, salicylate). Ψ decreased in the order Cl > Br > I > benzoate, salicylate consistent with conductometrically determined values for the counterion binding. HOED was also used to probe the microdomains formed in aqueous solutions of poly(dimethyldiallylammonium-*co*-methyl-*n*-dodecyldiallylammonium salts) containing different counterions (Copol C1-12 90/10 X). A similar dependence of Ψ on the nature of the counterion was found. Raising the temperature led to higher values of Ψ, while increasing the polysoap concentration appeared to lower the surface potentials for all polysoaps. With the exception of Copol C1-12 90/10 I and Sal, an additional peak in the UV-vis absorption spectrum of the probe was observed which was attributed to the aggregation of probe molecules on nondomain forming strains of the polysoap. Support for this conclusion was obtained from the observation that the intensity of the additional peak greatly decreased upon increasing the polysoap concentration. This behavior can be reconciled with the occurrence of a critical aggregation concentration. The sudden rise of the aggregation numbers of Copol C1-12 90/10 Br and benzoate at *ca.* 10 mM, leading to a constant value at higher concentrations, provides additional evidence for this conclusion.

Introduction

Polysoaps find important industrial applications as water thickeners in, *e.g.*, tertiary oil recovery.[1] They can also be used as alternatives for common surfactants as flocculants in the treatment of wastewater.[2] From a more fundamental point of view, the hydrophobic microdomains that are formed upon dissolving polysoaps in water at millimole per liter concentrations are of particular interest.

In previous studies, microdomains formed from Copol C1-12 90/10 Br were investigated.[3,4] The structure of this polysoap is

Copol C1-12 90/10 X   MDDAX
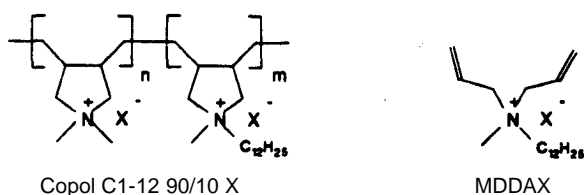
Detailed information on the size and structures of the microdomains formed by polysoaps of the type Copol C1-12 90/10 X is still lacking. Monitoring the value of the wavelength of maximum absorption of Methyl Orange[3] and measurements of the ratio of the intensities of the first and third vibronic peaks in the emission spectrum of pyrene[4] in the presence of polysoaps in aqueous solutions have shown that the micropolarity at the binding sites of the probes is greatly decreased as compared with water. Although strong evidence for the formation of microdomains has been found, no compelling evidence for a critical aggregation concentration (comparable to a critical micelle concentration) has been obtained.

In the present study we report surface potentials for hydrophobic microdomains of Copol C1-12 90/10 X (X = Cl, Br, I, benzoate (Ben), salicylate (Sal)) in aqueous solutions obtained by the method of Drummond *et al.*[5] This procedure is based upon the dependence of the pK_a of an aggregate-bound acid on the surface potential: the acid is more easily deprotonated when Ψ is more positive. Corrections for micropolarity effects on the dissociation process are taken into account by measuring the wavelength of the maximum absorbance of the acid (*cf.* Kosower's Z-value). Micelles formed from methyldiallyl-*n*-dodecylammonium salts (MDDAX, X = Cl, Br, I, Ben, Sal) were also probed for reference purposes. Counterion influences on micellar properties are reasonably well understood, and the influence of the nature of the counterion on the aggregation of the polysoaps can be rationalized. Furthermore, the aggregation numbers for Copol C1-12 90/10 with bromide and benzoate counterions have been studied as a function of polysoap concentration.

Experimental Section

Materials. Dimethyldiallylammonium bromide and Copol C1-12 90/10 Br were prepared according to standard procedures.[3,6] Copol C1-12 99/1, 98/2, 96/4, and 90/10 Cl were synthesized analogously from dimethyldiallylammonium chloride (Fluka AG) and methyldiallyl-*n*-dodecylammonium chloride (*vide infra*).

Methyldiallyl-*n*-dodecylammonium bromide was prepared according to a modified literature procedure.[3] Freshly distilled

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n-dodecyl bromide (Janssen Chimica, 0.12 mol) and 0.13 mol of methyldiallylamine were refluxed in 50 mL of anhydrous acetone for 3 days. The volatile components were removed under reduced pressure. The remaining oil was dissolved in 100 mL of water, and the aqueous layer was washed 5 times with 100 mL of diethyl ether. Traces of unreacted amine were azeotropically removed by evaporating the aqueous layer to dryness. The residue was dissolved in 50 mL of methanol, and the solution was boiled with activated charcoal for 15 min. After removal of the charcoal by filtration over Celite, the methanol was evaporated and the product was freeze-dried. The resulting oil became a hard solid after 6 months. The yield was 80%, lit.[3] 30%. The product was characterized by elemental analysis, and 200-MHz ^{1}H-NMR and 50-MHz ^{13}C-NMR (CDCl$_3$); NMR spectra were recorded using a Varian Gemini-200 NMR spectrometer. The ^{1}H-NMR spectrum corresponded to that described in literature.[3]

The surfactants MDDAX were prepared from methyldiallyl-*n*-dodecylammonium bromide by anion exchange. Copol C1-12 90/10 X was obtained from Copol C1-12 90/10 Cl in a similar way. A typical procedure was as follows: 100 g of DOWEX 1 × 8 Cl$^-$ anion exchange resin was washed with demineralized water and (successively) methanol until the eluent was colorless. To incorporate the desired counterion, the resin was stirred with 150 mL of a 4.5 M solution of the corresponding analytically pure sodium salt (Merck AG or Janssen) in water for at least 1 h. Then the salt solution was filtered off and the procedure was repeated twice. To remove any residual salt, the resin was washed with at least 5 L of demineralized water, using a glass filter (P3). The resin was suspended in 100 mL of demineralized water, and 10 (unit) mM of the desired compound was added to the slurry. After being stirred overnight, the mixture was filtered, and subsequently the filtrate was freeze-dried.

The purity and identity of the products were checked by elemental analysis, ^{1}H-NMR and ^{13}C-NMR (MDDAX only); an asterisk indicates a CH or CH$_3$ in the ^{13}C-APT (*vide infra*). NMR spectra were rather similar for MDDAHal and Copol Hal systems, respectively. The signals of the macromolecules all showed considerable line broadening and were similar to earlier examples described in literature.[3] The molecular weight of the benzoate copolymer was about 60000-80000, as was evidenced by time-of-flight mass spectrometry (TOFSPEC). On the basis of previous work,[3] the monomer ratios in Copols C1-12 99/1, 98/2, and 96/4 Cl could be safely assumed to approximately equal the feed ratios; unfortunately, these quantities could not be determined accurately using NMR spectroscopy.

Integration of relevant NMR resonances for organic counterion and polymer chain showed that the hydrophobic counterion exchange efficiency was at least 96% (based on the assumption that the monomer ratio was 9:1). From elemental analysis it was established that the iodide exchange efficiency for the polysoap was at least 91%. The absence of allylic signals indicated monomer removal to a degree of at least 95%.

MDDASal. ^{1}H-NMR (CDCl$_3$): *d* 0.84 (t, 3H), 1.21 (m, 18H), 1.55 (m, 2H, broad), 2.98 (s, 3H), 3.05 (m, 2H), 3.91 (m, 4H), 5.6 (m, 4H), 5.8 (m, 2H), 6.69 (m, 2H), 7.16 (m, 1H), 7.85 (dd, 1H). ^{13}C-NMR (APT, CDCl$_3$): *d* *14.06, 22.10, 22.61, 26.15, 28.95, 29.28, 29.51, 31.83, *47.34, 60.70, 63.54, 77.08 (t, CDCl$_3$), *116.15, *116.97, 120.37, *123.84, 129.64, *130.46, *131.91, 162.44, 173.42 (three CH$_2$ groups of the dodecyl chain remain unresolved because of overlap in the region near 28 ppm). Anal. Calcd for C$_{26}$H$_{43}$NO$_3$: C, 74.78; H, 10.38; N, 3.35. Found: C, 74.54; H, 10.10, N, 3.62.

MDDABen. ^{1}H-NMR (CDCl$_3$): *d* 0.85 (t, 3H), 1.20 (m, 18 H), 1.61 (m, 2H, broad), 3.1 (m, 2H), 3.21 (s, 3H), 4.2 (m, 4H), 5.7 (m, 4H), 5.9 (m, 2H), 7.27 (m, 3H), 8.05 (m, 2H). ^{13}C-NMR (APT, CDCl$_3$): *d* *14.06, 22.15, 22.62. 26.25, 29.01, 29.29, 29.50, 31.83, *47.49, 60.19, 63.41, 77.05 (t, CDCl$_3$), *124.34, *127.22, *129.31, 140.32, 171.74 (three CH$_2$ groups of the dodecyl chain remain unresolved because of overlap in the region near 28 ppm).

Anal. Calcd for C$_{26}$H$_{43}$NO$_2$: C, 77.75; H, 10.79; N, 3.49. Found: C, 77.86; H, 10.73; N, 3.55.

MDDABr. ^{13}C-NMR (APT, D$_2$O): *d* *30.30, 38.20, 39.06, 42.55, 45.44, 45.92, 46.01, 46.11, 46.23, 46.24, 48.39, *64.10, 76.86, 80.09, *140.86, 145.21 (two CH$_2$ groups remained unresolved because of overlap). Anal. Calcd for C$_{19}$H$_{28}$NBr: C, 63.32; H, 10.61; N, 3.89; Br, 22.17. Found: C, 62.95; H, 10.53; N, 4.17; Br, 22.25.

MDDAI: Anal. Calcd for C$_{19}$H$_{28}$NI: I, 31.2. Found: I, 31.9.

Copol C1-12 90/10 Sal: ^{1}H-NMR (D$_2$O): *d* 0.86, 1.16, 1.36, 2.10, 2.48, 3.03, 3.11, 3.16, 3.67, 6.91 (td), 7.38 (td), 7.83 (dd).

Copol C1-12 90/10 Ben: ^{1}H-NMR (D$_2$O): *d* 0.85, 1.24, 1.39, 2.15, 2.55, 3.05, 3.14, 3.17, 3.71, 7.47 (m), 7.88 (dd).

Conductometry. The onset of micellization of the monomeric surfactants MDDAX was indicated by a clear break in the conductivity *vs* [MDDAX] plots. Values of the degree of counterion binding (b) were calculated from the ratio of the slopes at surfactant concentrations below and beyond the critical micelle concentration (cmc);[7] in this approximation it is assumed that an increase of the surfactant concentration beyond the cmc only affects the conductivity of the solution through the free counterions (neglecting the contribution from the micelles to the conductivity), whereas at concentrations below the cmc the surfactants are dissociated, contributing to the solution conductivity as if they were strong electrolytes. Conductivities were measured using a Wayne-Kerr autobalance universal bridge, B642, fitted with a Philips platinum black electrode PW 9512/01 (cell constant 1.44 cm^{-1}). The temperature was kept constant to ±0.1 °C using a Lauda R2 electronic circulating water thermostat bath equipped with a magnetic stirring device. All solutions were thermostated for at least 15 min before starting the measurements. Surfactant concentrations were varied by adding 10-*m*L aliquots of a concentrated solution to the contents of the cell; concentrations were corrected for volume changes.

Surface Potentials. A slightly modified version of the method of Drummond *et al.*[5,8] was used to measure the surface potentials of the aggregates. Typically, 2 mg of 1-hexadecyl-4-[(oxocyclo-hexadienylidene)ethylene]-1,4-dihydropyridine (HOED, crystallized from ethanol) was dissolved in 200 *m*L of ethanol (UV grade, Merck), and 40 *m*L of the resulting solution was added to 10 g of the aqueous surfactant solution containing sodium hydroxide (pH 11.3). For MDDAX systems, the surfactant concentrations were chosen to exceed the cmc by about 5 mM to make sure that small changes in the surfactant concentration would not influence the value of Ψ. The mixture was allowed to equilibrate in the dark at the desired temperature for at least 4 h during which the color changed from orange to red for sufficiently hydrophobic aggregates. Surfactant solutions not containing any probe were used to run the background correction. By addition of small aliquots of a 1 M HCl solution, or 0.1 M HCl when the pH was between 9 and 7, the pH of the solution was gradually lowered without altering the surfactant or probe concentration. pH values were measured by dipping the electrode into the thermostated cuvette containing the solution and were equilibrated, so that these values were obtained at exactly the appropriate temperature. At each pH, the absorption spectrum was recorded from 300 to 600 nm; the apparent pK_a of the probe was determined by measuring the absorbance at the wavelength corresponding to the dissociated probe (typically, 490 nm) and using the equation pK_a = pH - log[$\alpha(1 - \alpha)^{-1}$], where α is the degree of dissociation of HOED = (Abs^{pHx}) / (Abs$^{pH10.0}$); there was no significant absorption of the undissociated probe at 490 nm, consistent with previous observations.[13] A range of pK_a values was determined at different pH values until the peak of the dissociated probe could not be clearly distinguished, then the whole experiment was repeated at least once and the mean value of all pK_a values was calculated. Surface potentials were calculated from Ψ = 2.303kT(pK_i - pK_a)/e where pK_i is the pK in the absence of charge, corrected for the micropolarity effect; e is the electronic charge. We used the pK_i values obtained by Drummond *et al.*; they measured pK_a values in water/dioxane mixtures characterized by different relative dielectric constants.[5]

An Orion Model 720 instrument fitted with a Radiometer GK2401 B glass electrode was used to measure the pH of the solutions. A Philips Model PU 8740 UV-vis scanning spectrophotometer equipped with a thermostated cell holder and a magnetic stirring device was employed to record the absorption spectra. Although the circulating water thermostat (Haake F3) could in principle stabilize the temperature to ±0.1 °C, in this case errors of 0.3 °C occurred because of feedback effects resulting from opening the spectrometer compartment when measuring

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Table 1. Surface Potentials and Micropolarities of Aqueous Micellar Systems at 25 ± 0.3 °C

compound	cmc (mM) (±0.1)	b (%) (±1)	[MDDAX]^a (mM)	l_{max} (nm) (±1)	e_r (±1)	pK_i (±0.02)	pK_{obs}	Ψ (mV)
MDDACl	15.6	50	21	489	33	9.51	7.47 ± 0.03	120 ± 2
MDDABr	10	63	15	492	31	9.58	7.78 ± 0.04	107 ± 2
MDDAI	4.8	68	10	495	28	9.63	7.87 ± 0.03	104 ± 2
MDDABen	5.7	75	10	485	36	9.44	7.95 ± 0.08	88 ± 5
MDDASal	1.7	91	7	486	35	9.46	8.09 ± 0.06	81 ± 4

^{a} MDDAX = methyl-*n*-dodecyldiallylammonium halide, benzoate, or salicylate.

Table 2. Surface Potentials of Aqueous Copol C1-12 90/10 X Systems at Different Concentrations and Temperatures

compound^a	[Copol] (mM)	temp^b (°C)	$l_{max}{}^c$ (nm)	$e_r{}^c$	p$K_i{}^c$	pK_{obs}	Ψ (mV)
Copol Cl	20	25				see text	
Copol Cl	50	25	487	35	9.48	7.83 ± 0.05	98 ± 3
Copol Cl	50	43	491	32	9.55	6.98 ± 0.06	161 ± 3
Copol Br	20	25	488	34	9.49	7.3 ± 0.2	136 ± 11
Copol Br	50	25	494	29	9.61	8.07 ± 0.03	91 ± 2
Copol Br	50	43	497	27	9.67	7.64 ± 0.06	127 ± 4
Copol I	20	43	500	23	9.73	7.69 ± 0.04	128 ± 2
Copol I	50	43	501	22	9.75	7.93 ± 0.02	115 ± 1
Copol Ben	20	25	481	40	9.36	7.57 ± 0.06	106 ± 4
Copol Ben	50	25	485	36	9.44	7.99 ± 0.05	86 ± 3
Copol Ben	50	43	488	34	9.49	8.03 ± 0.07	91 ± 5
Copol Sal	1.2	25				see text	
Copol Sal	10	25	483	38	9.40	8.00 ± 0.05	83 ± 3
Copol Sal	10	43	485	36	9.44	7.81 ± 0.02	102 ± 2
Copol Sal	20	25	484	37	9.42	8.31 ± 0.04	66 ± 2

^{a} Copol X = Copol C1-12 90/10 X. ^{b} Error: 0.3 °C. ^{c} For error limits, see Table 1.

the pH. The stirring device was not used while recording the spectra but only between the runs.

Aggregation Numbers. Steady-state fluorescence quenching according to the method by Turro and Yekta[9] was used to obtain the average number of dodecyl chains coming together in one aggregate (*N*) formed from Copol C1-12 90/10 Ben and Br at different concentrations. Pyrene was used as a donor; *N*-cetylpyridinium chloride (CPC) was the quencher. Since the equilibrium constant for binding of CPC to micelles from CTAB is high[10] (*K* = 83250), any electrostatic repulsion between quencher molecules and structurally similar aggregates formed from MDDAX or Copol C1-12 90/10 X is not expected to be a dominating factor in the binding process. The quencher concentration [Q] was varied while keeping the donor concentration constant (*viz.* ca. 2 × 10^{-6} M). Good duplicate results were obtained by stirring the solution while in contact with air for 15 min at the desired temperature at the beginning of each measurement; in this way the literature value of the aggregation number of SDS, *viz.* 63 ± 1,[11] could be exactly reproduced. At every value of [Q] the intensity *I* of the first vibronic peak of pyrene was measured; by plotting ln(*I_0*/*I*) *vs* [Q], *N* could be obtained from the slope *N*(C_D - cac)$^{-1}$. Deviations from linearity, probably because of polydispersity, were only obtained at the lowest values of [polysoap] and [Q]; in those cases the first two points were not taken into account. C_D equals the total surfactant concentration in unit M, I_0 is the intensity of the pyrene signal at zero [Q]. The critical aggregation concentration (cac) was assumed to be zero. As the aim of the experiment was only to show the presence of a break in the plot of *N* *vs* [polysoap], the inaccuracies arising from this assumption do not essentially affect the results. In addition, once the cac had been determined, a better approximation of the "real" values of the aggregation numbers could be obtained. However, we note that the application of steady-state fluorescence quenching for an accurate determination of aggregation numbers has serious limitations.[12] The main problem arises from the quenching rate constant not being fast enough (compared to the decay rate in the absence of quenchers) resulting in an underestimation of *N*. Fortunately this does not invalidate comparisons of aggregation numbers

obtained in this way, as the experimental errors are the same under these conditions. Furthermore we note that previously[3] reasonable values have been obtained for structurally similar amphiphiles.

An SLM Aminco SPF-500C spectrofluorometer equipped with a thermostated cell holder and a magnetic stirring device was used. Temperature control and variation of the quencher concentration were achieved in the same way as decribed previously for the conductometric measurements.

Results and Discussion

Surface Potentials of MDDAX Micelles. In Table 1 surface potentials of MDDAX surfactant micelles at 25 °C are summarized, together with values for the cmc and b. The surface potentials for the micelles with halide counterions have characteristic values for cationic surfactant assemblies.[13] Relative dielectric constants (e_r) were calculated from the corresponding wavelenghts of maximum absorption of dissociated HOED using the data in ref 5. These values are a measure of the micropolarity in the vicinity of the aggregates sensed by the bound probe. For the halide counterions, we find that b decreases in the order I > Br > Cl, and Ψ increases in the order I < Br < Cl. These trends can be explained by assuming that counterion binding involves relatively close proximity to the headgroups, requiring at least partial desolvation of the counterion. Since small ions are more strongly hydrated than large ones, their binding to the headgroups is less efficient.[14] Obviously, an increase of the counterion binding reduces the observed surface charge. Because of headgroup screening effects, the outer surface potential will be smaller when larger counterions are present.[15]

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Apparently, the Stern layer potential is measured instead of the real "surface" potential in the plane of the headgroups.

NMR spectroscopic results have shown that the hydrophobic counterions benzoate and salicylate are incorporated between the headgroups resulting in a sandwich-like structure.[16] This explains the extraordinarily high values of *b* and, concomitantly, the low values of Ψ in the case of these counterions. In the literature it has been tentatively assumed that salicylate ions are even better incorporated into the micelle because they possess an additional OH group that tends to be hydrated in order to lower its Gibbs energy. Therefore, salicylate ions have a higher tendency to reside close to the surface where there are less steric constraints for binding.[17]

Surface Potentials for Copol C1-12 90/10 X Microdomains. Table 2 presents the surface potentials at the microdomains formed by the polysoaps Copol C1-12 90/10 X. The rather high values are comparable with surface potentials of, *e.g.*, CTAB micelles reported in the literature.[15] We note, however, that the absolute magnitudes of all these potentials may be slightly affected by ion pairing effects.[15] Therefore we put our main emphasis on trends in the potentials as a function of the nature of the counterion. Comparisons for the halide counterions can best be made on the basis of data obtained at 43 °C for polysoap concentrations of 50 mM because at 25 °C and 20 mM polysoap concentration no evidence for a monomeric, dissociated probe could be obtained for Copol C1-12 90/10 Cl (*vide infra*). Similar trends as for the MDDAX surfactants are observed, although the variation of Ψ with the nature of X is larger for the polysoaps than for the micelles. Again, hydrophobic counterions are more efficiently bound to the aggregates than are halide counterions.

From these observations we conclude that electrostatic factors contribute to the hydrophobic domain formation of Copol C1-12 90/10 X polysoaps in a similar way as to the micellization of the structurally related monomeric surfactants. Again, it is probably the "polysoap Stern layer" that is being monitored, which is the "outer surface" where the ionic atmosphere starts to become diffuse.

Interestingly, Ψ decreases significantly upon increasing the polysoap concentration from 20 unit mM to 50 unit mM for Copol C1-12 90/10 bromide, iodide, and benzoate or from 10 to 20 unit mM in the case of Copol C1-12 90/10 Sal. This implies that the counterion binding to the microdomains becomes more efficient with increasing [Copol]. This is in accordance with the observation that I_{max} of HOED increases with increasing [Copol], indicating that the HOED binding sites exhibit more hydrophobic character at higher concentrations of polysoap.

At 25 °C the solubility of Copol C1-12 90/10 I in water is limited; apparently it behaves like a surfactant below its Krafft temperature. Only beyond 43 °C, an almost clear solution is obtained. For the other polysoaps, we observe that Ψ increases with increasing temperature. The increased mobility of the counterions and the increased distance between the counterions and the headgroups upon raising the temperature probably account for this effect.

Evidence for a Critical Aggregation Concentration. In the course of the surface potential measurements for MDDAI and MDDASal, almost "ideal" pH-dependent spectra were obtained with clear isosbestic points. However, with MDDACl, MDDABr, and MDDABen, an ad-
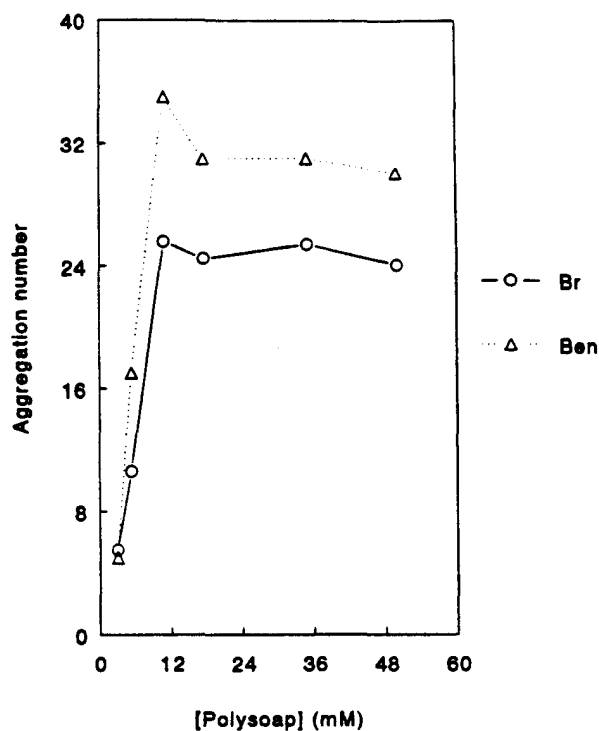
Figure 1. Mean aggregation number of Copol C1-12 90/10 X microdomains (X = Br, Ben) as a function of polysoap concentration.

ditional peak at 370 nm was found which did not disappear at any pH. Particularly with MDDACl this peak was large, whereas (at high pH) the absorbance of the dissociated HOED at *ca.* 490 nm was relatively low. Nevertheless Ψ values could still be determined. Quite unexpectedly, Copol C1-12 90/10 X polysoaps at 25 °C and 20 unit mM showed the same trend: when X = Sal or I (the latter at 43 °C) no additional peaks were observed, but for X = Cl only the 370 nm peak was present while this peak dominated the HOED spectrum in the presence of both Copol C1-12 90/10 Br and Ben. Consequently, Ψ could not be determined with great accuracy. We note, however, that at higher concentrations and at low concentrations for those cases where aggregation was supposedly most favorable, *viz.* when I⁻ or Sal were the counterions, no additional signals contributed to the spectrum. More weakly aggregating systems like Copol C1-12 *n/m* Cl (*n/m* = 99/1, 98/2, 96/4) did not show any "normal" HOED signals at all. These polysoaps are expected to aggregate even less favorably than Copol C1-12 90/10 Cl. Indeed, similar spectra were obtained. Now the question arose whether a nonaggregated HOED species was responsible for inducing the peak at 370 nm.[18] This was indeed borne out by experiment: the phenomenon turned out to be dependent on the polysoap concentration. For example, in the case of Copol C1-12 90/10 Cl at 50 unit mM a signal corresponding to "normal" dissociated HOED could be distinguished at high pH whereas at 20 unit mM only the 370-nm peak was present. With Copol C1-12 90/10 Br at 50 unit mM the "normal" signal even dominated the spectrum, whereas at 20 unit mM the reverse was observed. In this respect, Copol C1-12 90/10 Ben did not differ significantly from Copol C1-12 90/10 Br. When

(16) Unpublished results, *cf.* Underwood, A. L.; Anacker, E. W. *J. Colloid Interface Sci.* **1985**, *106*, 86.

(17) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley: New York, 1978.

(18) Dimerization might account for the observations, especially since this seems more likely to take place on a lineair chain than on a coil (in which monomers tend to be solubilized), *cf.* (a) Klotz, I. M.; Royer, G. P.; Sloniewsky, A. R. *Biochemistry* **1969**, *8*, 4752. (b) Quadrifoglio, F.; Crescenzi, V. *J. Colloid Interface Sci.* **1971**, *35*, 447. (c) Vitagliano, V. In *Aggregation Processes in Solution*; Wyn-Jones, E., Gormally, J., Eds.; Elsevier: Amsterdam, 1983.

Copol C1-12 90/10 Sal was probed, much lower concentrations (*ca.* 1 unit mM) had to be chosen in order to make the usual HOED signal disappear. Most significantly, no peak at 370 nm was present when HOED was dissolved in water in the absence of MDDAX or Copol additives (I_{max} = 382.4 nm at pH 11.3). Finally it must be noted that for the Copol C1-12 *n/m* Cl polysoaps still further peaks are present. At high pH, a peak at 372 nm dominates the spectrum. At low pH, a broad peak at 336 nm emerges. These observations can be rationalized by assuming "normal" acid-base behavior of unbound HOED in an aqueous salt solution. Alternatively, there might be a distribution of HOED oligomers that changes with pH.

We tentatively suggest that the concentration (and counterion) dependence of the observed phenomena strongly points to the presence of a critical aggregation concentration for the polysoap systems. Further support for this conclusion is found in the concentration dependence of the mean aggregation number (Figure 1). At a critical concentration the aggregation number increases steeply and remains almost constant at higher concentrations of polysoaps.

Finally, it should be noted that the aggregates may be formed either inter- or intramolecularly. Sau and Landoll have provided a schematic representation of intermolecular microdomains.[19] We envisage intramolecular aggregation as a "looping" of the polymer backbone with the hydrophobic groups coming together.

Supplementary Material Available: Representative spectra of HOED/MDDAC as a function of pH showing the occurrence of an isosbestic point (9 pages). Ordering information is given on any current masthead page.

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(19) Sau, A C.; Landoll, L. M. In *Polymers in Aqueous Media: Performance through Association*; Glass, J. E., Ed.; Advances in Chemistry Series No. 223; American Chemical Society: Washington, DC, 1989.