

Microcalorimetry of Polyelectrolyte–Micelle Interactions

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Received July 31, 1995. In Final Form: November 22, 1995

Polyelectrolytes interact with oppositely charged micelles to form soluble complexes, precipitates, or coacervates.¹ In the case of the polycation poly(dimethyl-diallylammonium chloride) (PDMDAAC) and the mixed micelle of sodium dodecyl sulfate (SDS) and Triton X-100 (TX100), soluble complexes are formed over a particularly wide range of conditions, thus allowing these complexes to be studied by turbidimetry, dynamic light scattering, static light scattering, electrophoretic light scattering, dialysis equilibrium, viscometry, and fluorescence.² The key system variables have been found to be ionic strength, I ; micelle composition (expressed as $Y = [\text{SDS}]/([\text{SDS}] + [\text{TX100}])$); polymer MW; polymer concentration, C_p ; and total surfactant concentration, C_s . The general conclusions reached are that (1) micelles complex with polymers when Y exceeds some critical value " Y_c "; (2) Y_c varies nearly linearly with $I^{1/2}$; (3) the structure of the complexes depends on polymer MW, C_p , and C_s , with large polymer concentrations and high MW leading to the formation of large aggregates (> 50 nm) that presumably contain several polymer molecules. However, in the case of low C_p and large C_s/C_p , intrapolymer complexes appear to form wherein the number of bound micelles can be as large as 1 for every ca. 30 polymer residues.²

Despite the large number of techniques applied to this system, few measurements supply direct information on the energetics of micelle–polymer binding. Limited observations of the binding isotherm have been made by dialysis methods,² but the experiments are complicated by the extraordinarily long times required to reach equilibrium, due to the size of the diffusing species (micelles). In fact, no explicitly thermodynamic measurements have been made on this system. However, microcalorimetry has been applied to at least one similar problem, the binding of SDS micelles to α,β -polysparthidrazide, a cationic polypeptide,³ and the results were used to generate micelle–polycation binding curves. It was thus of interest to extend this technique to the PDMDAAC–SDS/TX100 system, and the results form the subject of this report.

Experimental Section

PDMDAAC, nominal MW 2×10^5 , was a gift of Calgon Corporation (Pittsburgh, PA), commercial name "Merquat 100", and was dialyzed and freeze-dried before use. Although this polymer is highly polydisperse, recent studies conducted with narrow MW distribution fractions of PDMDAAC have shown rather little effect of MW distribution on the structure of the

complexes.⁴ SDS was electrophoretic grade, from Boehringer Mannheim (Indianapolis), and Triton X-100 was also electrophoretic grade, from EM Science.

Turbidity measurements were performed using a Beckman DU70 modified to accommodate a stirred 1 cm path length cell of our design. A Gilmont microburet was used to deliver SDS/TX100 to the polymer solution. In order to maintain constant polymer concentration, a second microburet was used to deliver a small aliquot of concentrated polymer solution with each addition of surfactant. Absorbance was read at 420 nm after equilibration, typically after 1 min. The results are reported as $100 - \%T$, which is nearly linear with the true turbidity in the transmittance range studied here.

Heats of mixing were measured with an isothermal heat-flux microcalorimeter with a detection limit of $<0.2 \mu\text{W}$ (Thermometric 2277 thermal activity monitor, Jarfalla, Sweden) and equipped with an optional flow-mix cell (2277–203, detection limit $0.5 \mu\text{W}$). With this device, two solutions are continuously pumped into the cell, thermally equilibrated, and then mixed within the detector. The resulting steady-state power signal, when corrected for heats of dilution, is proportional to the heat of reaction.

Solutions of polymer and surfactant were introduced into the calorimeter using two Microperpex peristaltic pumps set to deliver 2.5 and 7.5 mL per hour, respectively. The PDMDAAC concentration after mixing was 1.0 g/L. A series of mixed micelle solutions was prepared ranging from 2.3 to 52 g/L (4.2–95 mM) total surfactant. The mole fraction of SDS, relative to total surfactant, was $Y = 0.32$ in all cases, and the concentration of NaCl was 0.4 M. These conditions were chosen to be in the range of soluble complex formation (at this ionic strength, no complexes are formed below $Y = 0.23$, and bulk phase separation occurs at $Y > 0.37$). Calorimeter calibration was performed electronically using the 2277–121 calibration unit. The heats of dilution for the micellar solutions were measured by running each surfactant solution vs a polymer-free 0.4 M NaCl blank. The heats of dilution for PDMDAAC were found to be negligible.

Conversion of the calorimetric signal S in microwatts ($\mu\text{W s}^{-1}$) to the heat of reaction ΔH_{rx} in kilojoules per mole of polymer repeat unit was accomplished by the following equation

$$\Delta H_{rx} = 10^{-9} S (\text{FR})^{-1} (C_p)^{-1} m_0 \quad (1)$$

where FR is the flow rate (0.01 L/h), C_p is the polymer concentration (1.0 g/L), and m_0 is the molar mass per polymer repeat unit (162 g/mol).

Results and Discussion

Polyelectrolyte–micelle complexes may be formed in three ways: by the gradual addition of SDS to TX-100 micelles until $Y > Y_c$ (equivalent to charging up the micelles); by addition of micelles with $Y > Y_c$ to a polycation; and by the reverse addition. These procedures, all done at constant ionic strength, are referred to as type 1, type 2, and type 3 titrations, respectively. Calorimetric measurements were carried out as type 2 titrations, mixing PDMDAAC with SDS/TX100 micelles at constant Y and I . The results are shown in Figure 1, presented as ΔH_{rx} , the heat of reaction (reported as kJ mol^{-1} of polymer residue), vs total surfactant concentration.

The calorimetric data display the features of a binding curve, namely, a sigmoidal approach to an asymptotic value. Saturation of the polymer chains is achieved at a total surfactant concentration corresponding to ca. 50 ± 10 mM. The turbidimetric curve bears some resemblance to the calorimetric one, in regard to both the initial (relative) slope and the surfactant concentration corresponding to the limiting value (calorimetric) or the maximum (turbidimetric). This is remarkable, because the calorimetric result must reflect highly localized events, such as desolvation, while the turbidity measurements

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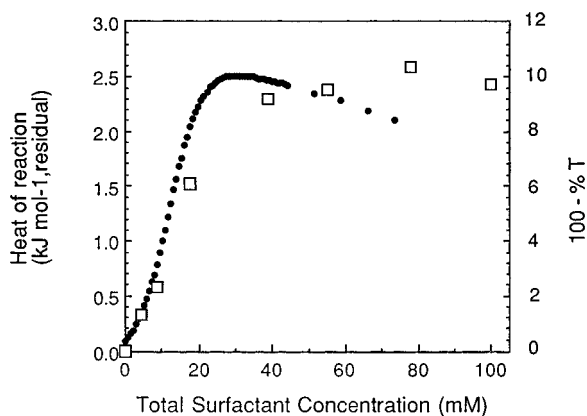


Figure 1. Type 2 titration of 1.0 g/L PDMDAAC with mixed micelles of SDS/TX100 ($Y = 0.32$), in 0.4 M NaCl: (\square) heat of binding (left axis); (\bullet) turbidity (right axis).

arise from the formation of large particles. If the structure of the complexes changed dramatically during the course of the type 2 titration, e.g. larger complexes forming at higher C_s/C_p , we would not expect the two curves to be so similar. The turbidimetric curve does in fact rise somewhat more steeply than the calorimetric curve and reaches a maximum prior to the calorimetric saturation point, but the two curves are virtually identical up to the 50% saturation point. The implication is that the structure of the complexes is invariant up to this point, so that an increase in the number of bound micelles corresponds not only to a proportional change in ΔH_{rx} but also to a parallel increase in the number of complexes, which in turn is linear with the intensity of scattered light (or turbidity). This suggests some degree of cooperativity: in the anticooperative case, where micelles are uniformly distributed over all polymer chains, structure should change strongly with degree of binding.

As saturation is approached, the turbidity rises steeply and passes through a maximum. Electrophoretic data⁵ suggest that the mobility of the complexes approaches zero in the vicinity of the turbidity maximum. Thus, progressive binding of micelles eventually leads to charge neutralization; and higher-order aggregation of these electrically neutral complexes leads to multipolymer complexes which scatter strongly.⁶ As saturation is approached, complexes acquire a net negative charge, aggregates dissociate, and the turbidity decreases, as shown in Figure 1 for $C_s > 30$ mM.

Other features of the turbidimetric titration curves also resemble the behavior of binding curves. As shown in Figure 2A, the initial slopes increase strongly with Y , presumably a reflection of the larger binding constants for micelles with larger surface charge densities. All curves show a decrease in turbidity at large surfactant concentration, attributable to a breakdown of large aggregates when micelle binding gives the complexes a negative charge. Prior to this region, a dramatic turbidity peak is observed when $Y > 0.32$, corresponding to

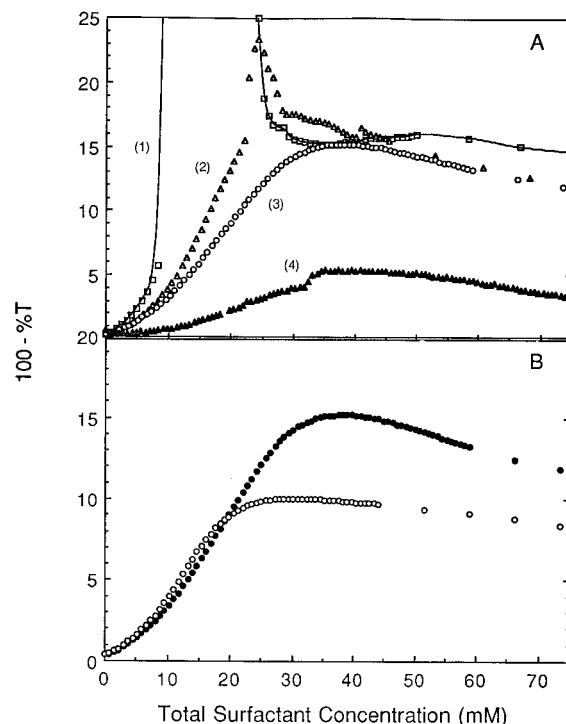


Figure 2. Type 2 turbidity titrations. (A) From left to right: (1) $Y = 0.40$, (2) 0.34 , (3) 0.32 , (4) 0.29 , all in 0.4 M NaCl, $C_p = 1.5$ g/L. (B) $C_p = 1.0$ g/L (\circ), 1.5 g/L (\bullet), both in 0.4 M NaCl, $Y = 0.32$.

coaggregation of electrically neutral complexes. That the initial slope is a reflection of the binding constant, hence Y alone, is supported by Figure 2B, which shows no influence of C_p on this slope. For $C_p = 1.0$ and 1.5 g/L, the maximum turbidities, τ_{max} , are 10 and 15, respectively, and the values of C_s at which the curves begin to display a decrease in slope, C_s' , are 17 and 25 mM (also in proportion 1:1.5), respectively. Thus, for the limited data available, both C_s' and τ_{max} appear to vary linearly with C_p . This observation is also consistent with the formation of scattering species of uniform size and mass whose number concentration increases linearly with C_p , which is implicit in the observation of normal Zimm plots obtained at polymer concentrations small compared to surfactant concentration.²

It is also of interest to note that ΔH_{rx} is positive; i.e., the binding of micelles to polymer is endenthalpic. This result suggests that the driving force for micelle binding is entropic, a conclusion also consistent with the observation that complexation is facilitated by an increase in temperature.⁷ While desolvation to some extent may accompany complex formation, the low turbidities of Figure 1 suggest that the complexes here are essentially soluble. Thus, the entropy gain on complex formation is best attributed to the release of small ions and is analogous to the increase in entropy when complexes are formed between oppositely charged polyelectrolytes, noted many years ago by Michaels.⁸

Acknowledgment. This work was supported by grant DMR9311433 from the National Science Foundation, jointly funded by the Divisions of Materials Research and Chemical Transport Systems.

LA950637+

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