

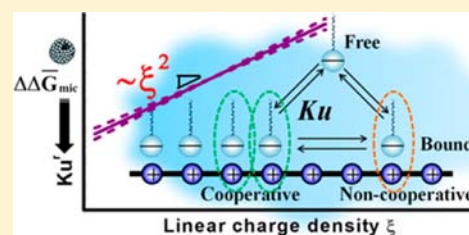
Universal Binding Behavior for Ionic Alkyl Surfactants with Oppositely Charged Polyelectrolytes

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S Supporting Information

ABSTRACT: Oppositely charged polyelectrolyte–surfactant mixtures are ubiquitous in biology and the basis of numerous consumer healthcare products. Despite their broad use, however, a rational approach to their formulation remains challenging because of the complicated association mechanisms. Through compilation and analysis of literature reports and our own research, we have developed a semiempirical correlation of the binding strength of surfactants to polyelectrolytes in salt-free mixtures as a function of the polyion linear charge density and the surfactant hydrophobicity. We have found that the cooperative binding strength increases as the square of the polyelectrolyte’s linear charge density and in proportion to the surfactant’s hydrophobicity, such that a quantitative relationship holds across a broad range of polyelectrolytes. Deviations from the correlation reveal the role of system-specific interactions not considered in the analysis. This engineering relationship aids in the rational design of oppositely charged polyelectrolyte–surfactant formulations for consumer products and biomedicines by enabling the prediction of binding strengths in polyelectrolyte–surfactant mixtures based on mesoscale parameters determined from the chemical composition.



1. INTRODUCTION

Mixtures containing polyelectrolytes (PEs) and oppositely charged amphiphilic surfactant molecules are long-standing subjects of scientific interest and industrial importance.^{1–8} Upon mixing of these charged species in solution, a strong association occurs, leading to the formation of PE–surfactant complexes (PSCs). These PSCs are of particular technological interest because of their appealing supramolecular structures (e.g., gels,^{4,9–11} liquid crystals,^{7,12–15} solid precipitates^{16,17}) and unique properties (e.g., gelation,^{4,9–11} tackiness,^{3,18} biodegradability,¹⁹ rheological and interfacial activity^{20,21}). One major application is for encapsulation of active hydrophobic compounds (e.g., antibacterial agents,⁹ drugs,^{22,23} functional oils^{10,24,25}), where these PSCs are formulated to achieve targeted storage, delivery, and controlled release. Such complex formulations must satisfy numerous criteria, and thus, there is significant interest in finding superior model systems as well as developing methods for their rational design.^{1–8} The complexation behavior generally depends on external solution properties^{26,27} (e.g., pH, temperature, solvent polarity, ionic strength, etc.) and many intrinsic chemical properties of the constituents^{28–32} (e.g., molecular weight, charge density, flexibility, hydrophobicity, etc.). As a result, developing robust engineering rules for the “predictable design” of PSCs with desired structural or physical properties is a highly desired but challenging research goal.

Identifying and quantifying the governing interactions between constituents in such solutions is an essential and necessary first step toward understanding and predicting the corresponding thermodynamic, mechanical, adhesive, optical,

electrical, and other properties that emerge from the PSC self-assembly. A structural model of polyion-induced micellization has been developed and found to offer a powerful rationalization for the complexation in many PE–surfactant mixtures.^{2,4,5,29,30,33–40} In this molecular association scenario, polyions act as counterions to the micelles by folding around them, similar to the conventional polyion–colloid interactions.^{2,30} Significant research in the literature has explored the role of molecular forces in forming polyion-dressed micelles by both theory and computation.^{2,4,5,29,30,33–40} The influence of hydrophobic interactions between polyions and micelles, polyion-mediated electrostatic interactions, and polyion-induced bridging forces between micelles have been clearly clarified. Of relevance to this micellization-based model, the simulation study by Wallin and Linse^{29,33} identified “polyion-mediated micelles” and explored the similarities in self-assembly of neat surfactant systems and PE–surfactant mixtures. Counterions of both the polyion and the charged micelles are largely expelled from the complex, such that the binding of oppositely charged surfactants to PEs can be, to a first approximation, visualized as an ion-exchange process where “condensed” counterions are replaced by surfactant.^{29,33} Hansson and co-workers^{5,38,40} have further pointed out a difference between “polyion-dressed” micelles and micelles surrounded by simple counterions, that strong repulsive forces stabilize the latter. A similar conclusion can be also drawn from the energetic expressions derived by Colby and co-workers^{35,36}

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Table 1. Summary of the PE–Surfactant Materials in Figure 1^a

ref	PE	surfactant	ref	PE	surfactant
Lapitsky ⁵³	JR-400 ⁵³	F ₇ C ⁷⁷	Liu ⁶⁵	PP50 ^{78–80}	C ₁₂ PCI ^{2,12,13}
	PSS ^{30,78}	DTAB ⁸¹		PP101 ⁷⁸	C ₁₂ PCI ^{2,12,13}
Hayakawa ^{51,61,71}	CMC ⁷¹	DTAB ^{81,82}		PP150 ⁷⁸	C ₁₂ PCI ^{2,12,13}
	alginate ⁷¹	DTAB ^{81,82}		KURROL ⁷⁸	C ₁₂ PCI ^{2,12,13}
	pectate ⁷¹	DTAB ^{81,82}	Treeby ⁶⁶	MAMMA3 ⁶⁶	C ₁₂ PCI ^{2,12,13}
	PAA ⁷¹	DTAB ^{81,82}		MASt ⁶⁶	C ₁₂ PCI ^{2,12,13}
	DNA ^{30,51,71}	DTAB ^{81,82}		MAMMA3 ⁶⁶	C ₁₆ PCI ^{52,80}
	CMC ⁷¹	TTAB ^{82,83}	Kosmella ⁵⁴	DADMAC–NMVA ⁵⁰	C ₁₂ PCI ^{2,12,13}
	alginate ⁷¹	TTAB ^{82,83}		DADMAC–NMVA ⁵⁰	C ₁₂ PCI ^{2,12,13}
	pectate ⁷¹	TTAB ^{82,83}		DADMAC–NMVA ⁵⁰	C ₁₂ PCI ^{2,12,13}
	PAA ⁷¹	TTAB ^{82,83}		DADMAC ⁵⁰	C ₁₂ PCI ^{2,12,13}
	DNA ^{30,51,71}	TTAB ^{82,83}		PAA ⁷¹	C ₁₂ PCI ^{2,12,13}
Mylonas ⁶²	PAM2 ⁸⁴	SDS ^{85–88}	Li ^{56,57,60}	DADMAC ⁵⁰	SDS ^{85–88}
	PAM6 ⁸⁴	SDS ^{85–88}		AMD2 ^{50,84}	SDS ^{85–88}
	PAM21 ⁸⁴	SDS ^{85–88}		AAD ^{50,84}	SDS ^{85–88}
Kasseh ⁶³	AMPSAM ^{30,84}	BDDAB ^{89,90}		AMD1 ^{50,84}	SDS ^{85–88}
	AMPS20AM ^{30,84}	BDDAB ^{89,90}		JR400 ⁵³	SDS ^{85–88}
Okuzaki ^{52,58,64}	PAMPS ^{30,84}	C ₁₂ PCI ^{79,80}		DADMAC ⁵⁰	SLE ₃ S ^{91,92}
	PAMPS ^{30,84}	C ₈ PCI ^{45,79}		AMD2 ^{50,84}	SLE ₃ S ^{91,92}
	PAMPS ^{30,84}	C ₁₀ PCI ⁷⁹		AAD ^{50,84}	SLE ₃ S ^{91,92}
	PAMPS ^{30,84}	C ₁₂ PCI ^{52,79}		AMD1 ^{50,84}	SLE ₃ S ^{91,92}
	PAMPS ^{30,84}	C ₁₆ PCI ^{52,79}		JR400 ⁵³	SLE ₃ S ^{91,92}
	PAMPS ^{30,84}	C ₁₈ PCI ⁹³		DADMAC ⁵⁰	SDBS ⁵⁹
Matulis ⁴⁷	DNA ^{30,51,71}	C ₉ H ₂₁ N ^{47,94,95}		AMD2 ^{50,84}	SDBS ⁵⁹
	DNA ^{30,51,71}	C ₁₀ H ₂₃ N ^{47,94,95}		AAD ^{50,84}	SDBS ⁵⁹
	DNA ^{30,51,71}	C ₁₁ H ₂₅ N ^{47,94,95}		AMD1 ^{50,84}	SDBS ⁵⁹
	DNA ^{30,51,71}	C ₁₂ H ₂₇ N ^{47,94–96}		JR400 ⁵³	SDBS ⁵⁹
	DNA ^{30,51,71}	C ₁₃ H ₂₉ N ^{47,94,95}		DADMAC ⁵⁰	SDBS ⁵⁹

^aNotation: PSS, poly(styrene sulfonate); DDAB, dodecyltrimethylammonium bromide; F₇C, sodium perfluorooctanoate; PP, sodium polyphosphate; AMPS, copolymers of acrylamide and sodium-2-acrylamido-2-methylpropanesulfonate; BDDAB, benzyltrimethylammonium bromide; PAMPS, poly[2-(acrylamido)-2-methylpropane sulfonic acid]; C₈PCI, *N*-decylpyridinium chloride; C₁₀PCI, *N*-cetylpyridinium chloride; C₁₂PCI, *N*-dodecylpyridinium chloride; C₁₆PCI, *N*-cetylpyridinium chloride; C₁₈PCI, *N*-octadecylpyridinium chloride; C₉H₂₁N, *N*-nonylamine; C₁₀H₂₃N, decylamine; C₁₁H₂₅N, undecylamine; C₁₂H₂₇N, dodecylamine; C₁₃H₂₉N, tridecylamine; MASt, poly(maleic acid-*co*-styrene); MAMMA, poly(maleic acid-*co*-methyl methacrylate); MAVA, poly(maleic acid-*co*-vinyl acetate) (MAVA); JR400, *N,N,N*-trimethylammonium derivative of hydroxyethyl cellulose chloride; AMD1 and AMD2, poly(acrylamide-*co*-diallyldimethylammonium chloride); AAD, poly(acrylic acid-*co*-diallyldimethylammonium chloride); DADMAC, poly(diallyldimethylammonium chloride).

for surfactant micelle formation in the presence of PEs, where the role of counterion condensation was again considered. Other recent studies have addressed the role of “complex salts” (ionic surfactant/polyion complexes) on the equilibrium thermodynamics and interactions in PSC mixtures. Ion substitution from simple to polymeric counterions leads to effectively increasing attractions between surfactant micelles, condensing these “polyion-dressed” micelles into a concentrated phase.^{16,17}

Numerous studies have reported the inclusion of additional molecular details to further explore the effects of specific molecular interactions within this polyion micelle framework.^{37,41,42} These studies have established a molecular-level picture of the surfactant micellar aggregation behavior (e.g., aggregation size and shape)⁴ for the specific system considered. However, there is a need for a broader approach when seeking to formulate to achieve targeted properties. As noted by Flory, “...better agreement with experiment doubtless can be achieved with a more refined theory, but the improvement thus gained may be at a considerable sacrifice of simplicity...It may be more fruitful to adopt a simpler treatment of reasonable generality at the sacrifice of representation of individual cases.”⁴³ Thus, with these important studies^{2,4,5,29,30,33–40} as background, we seek correlations that reasonably unify and summarize relationships

between molecular forces and chemistry over a broad range of oppositely charged PE–surfactant mixtures.

Our view is reductionist in that a thermodynamic description of surfactant binding onto PE chains is identified as a primary, almost unavoidable step toward understanding the overall complexation behavior of PE–surfactant mixtures.^{28,30,44–46} Of particular value are experimental measurements of PE–surfactant binding enthalpy within the context of a thermodynamic model for the binding Gibbs free energy.^{10,47,48} We consider the molecular forces relevant for surfactant binding onto PE chains generally to be dominated by two contributions, namely, the electrostatic force (with the associated entropy gain upon counterion release⁴⁷) and the hydrophobic force (with the associated entropy gain upon liberation of unfavorably structured water^{47,49}). These forces have been intensively studied in the literature and shown to be significant for PE–surfactant mixtures upon binding,^{28,47,50–53} and they can be quantified by measuring the binding affinity.^{10,47,48} Indeed, measuring the binding isotherm (e.g., the fraction of PE binding sites that are occupied by surfactant molecules) is a convenient and established method to gain understanding of the molecular interaction affinity in a PE–surfactant mixture.^{28,30,44–46} Such binding has been shown to be highly cooperative in nature because of the preferred aggregation of

surfactant on PEs.⁵⁴ Several binding isotherms have been derived for the binding of surfactants onto PE chains.^{28,30,44–46} A commonly used, simple, but robust model that describes surfactant binding in many PE–surfactant mixtures is the Satake–Yang model,⁴⁴ which is based on the Zimm–Bragg theory.⁵⁵ In this model, the PE chain is treated as a one-dimensional lattice with a fixed number of binding sites for surfactants. Sites are characterized as either individual or cooperative binding, and surfactant can interchange between them.^{53,56,57}

In this work we focus on the PE's linear charge density and surfactant's hydrophobicity as the most relevant, coarse-grained properties. Observations in the literature of surfactant binding to PE chains support this choice of coarse-grained properties.^{28,47,50,52,58,59} For example, larger binding affinity was found in PE–surfactant mixtures with greater PE charge density^{28,47} or more hydrophobic groups.^{47,59} Consequently, compiling and summarizing observations of binding in terms of these properties turns out to be useful to deduce rules for formulating PSCs.

Surfactant binding to PEs can be quantitatively measured by analyzing experimental data [e.g., potentiometric titrations^{28,50} and isothermal titration microcalorimetry (ITC)^{47,53}] using an extension of the two-energy-state model of Satake and Yang.⁴⁴ In previous work, we demonstrated a method to quantify the binding enthalpy by ITC and thereby to quantify the strength of electrostatic and hydrophobic interactions for a systematic series of PE–surfactant mixtures.^{56,57,60} Although the Satake–Yang model is an idealization of the actual process of aggregation of surfactants onto PEs that, for example, considers only nearest-neighbor interactions and neglects steric effects, it leads to a robust model isotherm that is useful for extracting quantitative binding measurements from experiment. Further, Hansson and Almgren²⁸ showed that the self-aggregation behavior (e.g., the aggregation number) in general reflects the slope of the cooperative binding isotherm, providing a link to more structurally accurate micellization-based models. Our goal here is to compile the literature values for the cooperative binding strength and determine the dependence on the two aforementioned coarse-grained system properties, where the former are often analyzed in the literature within the framework of the Satake–Yang model. The outcome of such experiments of relevance here is the intrinsic cooperative binding strength parameter Ku . This intrinsic binding strength has been reported by numerous authors for a wide variety of salt-free PE–surfactant mixtures in the literature (as listed in Table 1)^{47,50–54,56–58,60–66} and thus conveniently serves as an intrinsic property characteristic of surfactant binding for each specific system. Ultimately, determining how this binding strength parameter governs the solution thermodynamics and the microstructure of the PSCs is desired for the rational formulation of PSCs with specific properties, such as elastic modulus⁶⁷ and tackiness.^{3,18} To date, there is no general predictive method for formulating specific microstructures in PSCs, especially highly ordered structures such as cubic, cylindrical, hexagonal, and lamellar morphologies,^{7,68,69} and their associated properties,^{8,68,70} yet it is reasonable to expect that all of these depend fundamentally on the strength of the cooperative binding of the surfactant to the polyelectrolyte.

The goals achieved in the present work are multifold. We broadly survey the binding strengths reported in the literature across a wide variety of mixtures of ionic alkyl surfactants with PEs of opposite charge, and in doing so we identify a

semiempirical correlation between the cooperative binding strength and the surfactant hydrophobicity and PE linear charge density. Analysis of the results also enables an exploration of the molecular physics underlying the binding behavior for specific systems, which leads to interesting scientific questions for further research.

2. RESULTS AND DISCUSSION

Unified Binding Behavior. In the following, we generalize the binding behavior of PE–surfactant mixtures with opposite charges by examining the cooperative binding constant ($Ku_{l,\text{exp}}$) determined over a variety of salt-free PE–surfactant mixtures from our work and literature reports.^{47,51–54,56–58,60–66,71} These $Ku_{l,\text{exp}}$ values are reported for systems that are relevant to foods, pharmaceuticals, and cosmetics, and these systems are summarized in Table 1. They include polycations and polyanions. It should be noted that these $Ku_{l,\text{exp}}$ values were determined using several techniques, including potentiometric titrations as well as ITC; however, all of the binding data reported here are based on the Satake–Yang model interpretation without exception, and only simple alkyl chain surfactants were considered. The data taken in our laboratory are for equilibrium PSC formation,⁵⁶ and we can only assume the same for the literature data. However, it is worth cautioning that nonequilibrium states are common for PSCs.⁷² Further information concerning these data is reported in Table SI.1 in the Supporting Information, where the values, relevant assumptions, and references for each system are listed.

Figure 1 shows the reported $Ku_{l,\text{exp}}(T,\xi)$ parameters as a function of the charge on the PE, as characterized by the

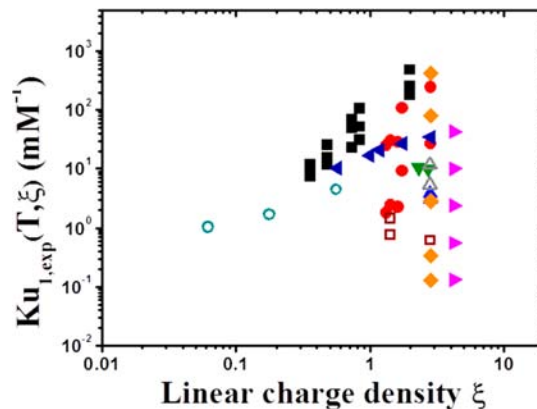


Figure 1. Experimentally reported binding strengths $Ku_{l,\text{exp}}(T,\xi)$ as a function of the reduced linear charge density of the polyon, ξ . (black ■) Li; (red ●) Hayakawa; (purple ▲) Liu; (green ▼) Kasseh; (orange ◆) Okuzaki; (blue left-pointing triangles) Kosmella; (pink right-pointing triangles) Matullis; (brown □) Treeby; (light blue ○) Mylonas; (gray △) Lapitsky.

reduced linear charge density, ξ , which is the “ideal” linear charge density of the PE chain. The reduced linear charge density is a dimensionless value describing both the geometry and charge density of the PE chain, and it is defined in eq 1:

$$\xi = \frac{l_B}{b} \quad (1)$$

where l_B is the Bjerrum length ($l_B = e^2/4\pi\epsilon k_B T = 0.71$ nm in water at 25 °C) and b is the average linear distance between neighboring charges along a fully stretched PE chain. The

charges are expected to be statistically distributed on the polyion. Here we used the definition given in eq 1 to describe the ideal PE linear charge density, similar to the one given by Hansson and Almgren.²⁸ This definition does not consider Manning counterion condensation,⁷³ as the condensed counterions are largely replaced by surfactants upon binding⁴ and thus are not relevant.

The interaction energies in Figure 1 are observed to vary over 4 orders of magnitude. In view of the broad range of chemistries explored, it is not surprising that these $Ku_{1,\text{exp}}(T, \xi)$ values spread over orders of magnitude and exhibit no readily apparent trend. The PEs under consideration also yield a very broad range of reduced PE linear charge densities, from weakly charged cellululosic polymers to synthetic copolymers and highly charged DNA.

Surfactant self-assembly facilitated by the PE can be conceptually related to surfactant micellization in solution, and $Ku_{1,\text{exp}}(T, \xi)$ characterizes the strength of this cooperative binding. As this binding is driven primarily by hydrophobic interactions for a given PE charge density, the $Ku_{1,\text{exp}}(T, \xi)$ values can be further analyzed and understood on the basis of the surfactant's intrinsic hydrophobicity as follows. The micellization free energy ($\Delta\bar{G}_{\text{mic}}$) in water has been reported for each of the hydrophobic alkyl surfactants under consideration.⁴⁹ We use this intrinsic micellization free energy as a reference state for the intrinsic binding strength, thereby accounting for the differences in the intrinsic hydrophobicities of the surfactants upon binding (for details, see section SI.1 in the Supporting Information). Thus, we propose to unify the binding strengths $Ku_{1,\text{exp}}(T, \xi)$ using these intrinsic micelle free energies by rescaling all of the reported $Ku_{1,\text{exp}}(T, \xi)$ parameters for the mixtures in Table 1 to a reference system, sodium dodecyl sulfate (SDS), as shown in eq 2:

$$Ku_{1,\text{exp}}^r(T_0, \xi) = \frac{Ku_{1,\text{exp}}(T_0, \xi)}{\exp\left(-\frac{\Delta\bar{G}_{\text{mic},1}(T_0) - \Delta\bar{G}_{\text{mic},\text{SDS}}(T_0)}{RT_0}\right)} \quad (2)$$

in which the rescaled binding strength parameter is denoted as $Ku_{1,\text{exp}}^r(T_0, \xi)$.⁶⁰ It should be noted that this empirical rescaling is consistent with relationships in the literature between the critical aggregation concentration (cac) in polyion solution and the critical micelle concentration (cmc) in polyion-free solution.^{35,36} As shown in a separate experimental report,⁶⁰ this rescaling can be derived under the assumption that $-RT \ln \bar{K}u = RT \ln x_{\text{cac}}$ where $\bar{K}u$ is the dimensionless Ku [given by $\bar{K}u \approx 55556 \text{ (mM)} \times Ku \text{ (mM}^{-1}\text{)}$] and x_{cac} is the mole fraction of surfactant at the cac. To apply the rescaling, it was also necessary to correct for the small temperature differences in the binding data, so all of the data are scaled to a reference temperature (T_0) of 298 K. Further details concerning the temperature correction and rescaling are given in section SI.1 in the Supporting Information.

Figure 2 summarizes the rescaled interaction parameters $Ku_{1,\text{exp}}^r(T_0, \xi)$ from eq 2, which are plotted as a function of the reduced linear charge density. With rescaling, the data collapse onto a master curve with an interesting power-law behavior, which is even more surprising considering the large variation in the chemistries and broad range of sources of the data. The data taken on a systematic set of PEs and surfactants in our laboratory (black squares in Figure 2) were used to define the correlation with a 95% prediction interval.⁶⁰ All of the experimental data from the literature fall within a 95% interval

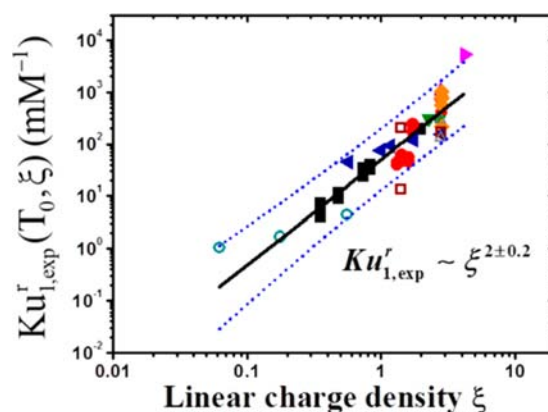


Figure 2. Experimentally reported binding strengths $Ku_{1,\text{exp}}(T, \xi)$ rescaled to the reference system SDS, $Ku_{1,\text{exp}}^r(T_0, \xi)$, as a function of the polyion reduced linear charge density ξ . (black ■) Li; (red ●) Hayakawa; (purple ▲) Liu; (green ▼) Kasseh; (orange ◆) Okuzaki; (blue left-pointing triangles) Kosmella; (pink right-pointing triangles) Matullis; (brown □) Treeby; (light blue ○) Mylonas; (gray △) Lapitsky. (black ■) Li; (red ●) Hayakawa; (purple ▲) Liu; (green ▼) Kasseh; (orange ◆) Okuzaki; (blue left-pointing triangles) Kosmella; (pink right-pointing triangles) Matullis; (brown □) Treeby; (light blue ○) Mylonas; (gray △) Lapitsky. The black solid line is the power-law regression, and the blue dotted lines show the 95% prediction interval.

(notably, a statistically equivalent correlation was found when the complete data set was used for the fitting, as given in Figure S.1 in the Supporting Information).

A number of assumptions were unavoidable in performing this rescaling and may account for some of the observed deviations. The most significant source of uncertainty is that the micelle free energies were calculated from a mass-action model (eq 5 in section SI.1 in the Supporting Information), which requires knowledge of the cmc as well as the degree of ion disassociation α . Both of these data sources have measurement uncertainties. Furthermore, the reduced linear charge density parameters were calculated using the “ideal” definition requiring the average linear distance between charges. Some of these had to be estimated directly from the polymer chemistry. Table SI.1 in the Supporting Information documents the values used in this work. Deviations are more significant for the highly charged systems, especially for DNA molecules, as shown in Figure 2. This may be explained in part by the strong patch-charge attractions that exist at low ionic strength in highly charged PE–colloid solutions, whereas the weakly charged systems seem to form more homogeneous interactions.^{2,74} Such “patches” are excluded in the simplified Satake–Yang model interpretation, and therefore, deviations can be anticipated. Other possible reasons for these deviations are discussed in detail in the following.

The scaled $Ku_{1,\text{exp}}^r(T_0, \xi)$ values exhibit an intriguing power-law dependence on the linear charge density parameter with a slope of 2.0 ± 0.2 in a log–log plot, indicating that $Ku_{1,\text{exp}}^r(T_0, \xi) \propto \xi^2$. Thus, we can deduce from this semiempirical correlation that the unified PE–surfactant cooperative binding strength has a squared-power dependence on the PE charge density, whereas the magnitude of the binding strength is quantitatively determined by the surfactant hydrophobicity.

We are unaware of any theoretical prediction of this squared-power dependence of the cooperative binding strength on the linear charge density parameter. However, such a dependence is plausible from simple geometric arguments. Although

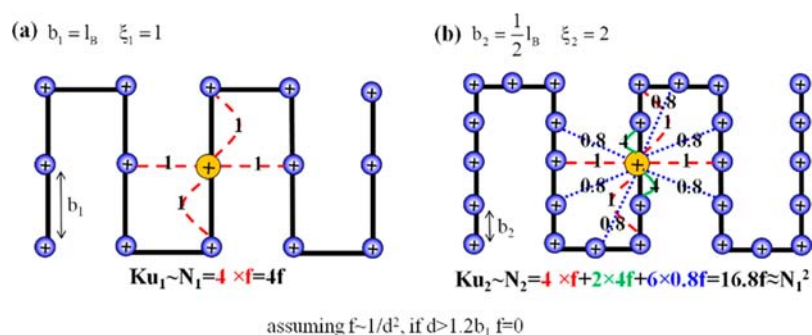


Figure 3. Schematic illustration showing how doubling the linear charge density of a PE chain leads to a possible quadrupling of the intrinsic interaction strength for a single site. f represents the energies of interaction between surfactants bound to the site (marked by yellow) and surrounding sites; f is assumed to be proportional to the inverse square of the distance to be negligible if the distance between the two sites is larger than $1.2b$.

$Ku_{i,\text{exp}}^r(T_0, \xi)$ is determined from a binding isotherm without structural information, one can consider the polyion-mediated micellization model in the literature, in which a PSC consists of a PE chain wrapped around a surfactant micelle, such as shown by simulations.^{29,33} For a given PE, the length of PE that can bind to a given micelle is proportional to the surface area of the micelle.^{5,29} Therefore, increasing the linear charge density of the PE chain while leaving the micelle fixed should linearly increase the number of interactions for a fixed polymer coverage but not change the inherent strength of cooperative binding per surfactant. The stronger squared-power dependence observed in the correlation then suggests a cooperative effect whereby the increase in linear charge density on the polyelectrolyte must also increase the aggregation number of the PE–surfactant aggregates that constitute the PSCs. Consistent with this hypothesis, Hansson and Almgren reported that the aggregation number of cetyltrimethylammonium bromide (CTAB) micelles increases from 43 in solutions of sodium (carboxymethyl)cellulose with a charge density of $\xi = 0.8$ to 62 for $\xi = 3.0$.²⁸ The squared-power dependence means that halving the distance between charge sites along the PE must quadruple the strength of the molecular interactions that give rise to this cooperative binding strength. It is tempting to speculate that such a dependence trivially follows from the squared-power dependence of the charge density per unit surface area in a model where the PE is close-packed on a relatively flat surface at a fixed molar area density. Figure 3 presents a schematic illustration of this geometric effect showing that the observed correlation is plausible. Obviously the PSC structure is much more complex. However, this naïve drawing suggests that cooperative rearrangement of the aggregate microstructure with increasing PE charge density could be the source of the observed scaling behavior. Indeed, the surfactant microstructure in the PSC generally becomes more ordered with increasing charge density. In a related work,⁶⁰ this microstructural evolution with increasing charge density has been explored further through X-ray and small-angle neutron scattering studies of a series of model PSC mixtures.

Semiempirical Model. On the basis of the novel scaling law, we further deduce a semiempirical equation for predicting the cooperative binding strength for ionic surfactants binding with oppositely charged PEs more generally. Specifically, this simple model provides a measure of the binding strength in terms of the polyion's linear charge density and the

hydrophobicity of the surfactant. Thus, we propose the following relationship:

$$\ln Ku_{1,\text{pre}}(T_0, \xi) = - \frac{\Delta(\Delta\bar{G}_{\text{mic}}(T_0))_{1-\text{SDS}}}{RT_0} + \ln Ku_{1,\text{exp}}^r(T_0, \xi) \quad (3)$$

in which $Ku_{i,\text{pre}}(T_0, \xi)$ is the predicted Ku value. It should be noted that the prefactor in $\bar{K}u$ has been canceled, allowing eq 3 to be written in terms of Ku for simplicity.

Experimentally, $Ku_{i,\text{exp}}^r(T_0, \xi)$ is reasonably described by the empirical power-law expression as described in Figure 2. Further substitution of the mass-action model for the free energy of micellization of an ionic surfactant, $\Delta\bar{G}_{\text{cmc}} = RT(2 - \alpha) \ln x_{\text{cmc}}$ ⁴⁹ into eq 3 leads to the semiempirical model for $Ku_{i,\text{pre}}(T_0, \xi)$ based on parameters directly determined from the chemical composition (i.e., ξ , x_{cmc} and α), which is given in eq 4:

$$\begin{aligned} \ln Ku_{1,\text{pre}}(T_0, \xi) &= - \frac{\Delta(\Delta\bar{G}_{\text{mic}}(T_0))_{1-\text{SDS}}}{RT_0} + \ln(A\xi^N) \\ &= - \ln(x_{\text{cmc},1})^{2-\alpha(T_0)} \\ &\quad + \ln(x_{\text{cmc},\text{SDS}})^{2-\alpha_{\text{SDS}}(T_0)} + \ln(A\xi^N) \end{aligned} \quad (4)$$

where the constants $A = 50.8 \pm 6.9$ and $N = 2.0 \pm 0.2$ were determined from the empirical power-law fit and are referenced to SDS [$Ku_{i,\text{exp}}^r(T_0, \xi)$] at 298 K, α is the ion dissociation proportion for surfactant micellization, and x_{cmc} is the mole fraction of surfactant at the cmc in polyion-free solution. These parameters are summarized in Table SI.1 in the Supporting Information. Figure 4 is an engineering plot demonstrating the correlation between the experimental $Ku_{i,\text{exp}}(T_0, \xi)$ values and the predicted $Ku_{i,\text{pre}}(T_0, \xi)$ values, where good agreement is observed across the entire range of parameter space with no systematic deviations.

Effect of PE Chain Stiffness and Hydrophobicity. It is anticipated that other material properties, including the PE chain stiffness,^{30,33} hydrophobicity,^{36,42} or molecular weight,⁴⁶ also affect the strength of the binding interactions in PE–surfactant mixtures. For instance, as reported by Dubin and co-workers,³⁰ surfactant binding was generally weaker for a stiffer PE chain relative to a more flexible polymer with the same linear charge density. Similar results were shown by the simulations of Wallin and Linse.³³ These factors were not explicitly included in formulating the general correlation, and

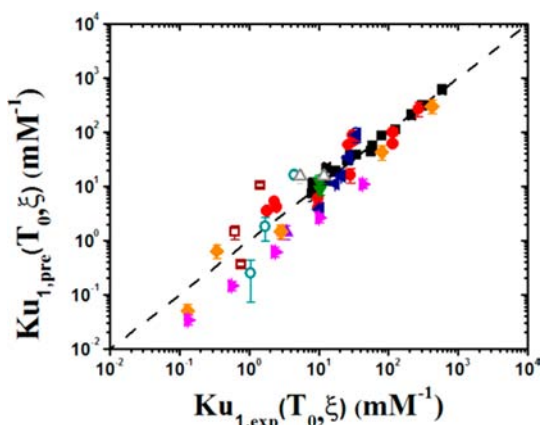


Figure 4. Engineering correlation plot of the experimentally reported binding strengths $Ku_{1,exp}(T_{0,\xi})$ vs. the binding strengths $Ku_{1,pre}(T_{0,\xi})$ predicted using eq 4 at 25 °C. (black ■) Li; (red ●) Hayakawa; (purple ▲) Liu; (green ▼) Kasseh; (orange ◆) Okuzaki; (blue left-pointing triangles) Kosmella; (pink right-pointing triangles) Matullis; (brown □) Treeby; (light blue ○) Mylonas; (gray △) Lapitsky.

therefore, it is possible to explore the possible influence of these factors by examining deviations from the predicted binding strengths. Therefore, we looked for any systematic trends in the quantitative deviation between the experimentally measured cooperative binding strengths $Ku_{1,exp}(T_{0,\xi})$ and the correlation values $Ku_{1,pre}(T_{0,\xi})$. To accomplish this, we compiled from the literature or, when necessary, estimated the intrinsic stiffness

(i.e., persistence length) and hydrophobicity of each poly-electrolyte, and these values are given in Table 2. The details of the assumptions and procedures used for obtaining these factors are shown in section SI.3 in the Supporting Information. In Figure 5, the deviations between the predicted $Ku_{1,pre}(T_{0,\xi})$ and experimental values are plotted against (a) the PE chain intrinsic persistence length ($l_{p,0}$) (characterizing the chain stiffness) and (b) the octanol–water partition coefficient $\text{Log}K_{ow}$ (representing the chain hydrophobicity). The deviations show no apparent trends with respect to either PE chain stiffness or chain hydrophobicity. This suggests that given the uncertainties in the data itself, the proposed model reasonably represents the cooperative binding behavior and there are no additional systematic dependences on PE chain stiffness or hydrophobicity.

Although no obvious trends with PE persistence length or hydrophobicity are evident, additional insights concerning specific systems can be deduced from Figure 5. For instance, the DNA solutions exhibit systematically large ($\sim 300\%$) positive deviations in binding strengths from the correlation. Crystalline or highly ordered self-assembled surfactant aggregates are frequently reported in such systems.^{11,12,16,75,76} Such significant changes in the state of surfactant aggregation can be expected to influence the cooperative binding parameter Ku . As also suggested by Hansson and Almgren,²⁸ the free energy of forming a PSC is reflected in both the aggregation number and the intrinsic binding strength for a given PE–surfactant mixture. In related work, we have also demonstrated

Table 2. Summary of PE Chain Stiffnesses and Hydrophobicities Used in the Deviation Plots in Figure 5

ref	PE	surfactant	$\text{Log}K_{ow}^a$	$l_{p,0}$ (nm) ^b	ref	PE	surfactant	$\text{Log}K_{ow}^a$	$l_{p,0}$ (nm) ^b
Lapitsky ⁵³	JR-400	F ₇ C	0.8	3 ⁹⁷	Liu ⁶⁵	PP50	C ₁₂ PCI	−0.8	31 ⁹⁸
	PSS	DTAB	0.8	3 ³⁰		PP101	C ₁₂ PCI	−0.8	31 ⁹⁸
Hayakawa ^{51,61,71}	CMC	DTAB	−2.3	5 ²⁰		PP150	C ₁₂ PCI	−0.8	31 ⁹⁸
	alginate	DTAB	−2.3	13 ⁹⁹	Treeby ⁶⁶	KURROL	C ₁₂ PCI	N/A	N/A
	pectate	DTAB	−2.3	13 ¹⁰⁰		MAMMA3	C ₁₂ PCI	0.9	10.8 ¹⁰¹
	PAA	DTAB	0.33	1 ¹⁰²		MASt	C ₁₂ PCI	1.2	10.8 ¹⁰¹
	DNA	DTAB	−2.3	50 ^{30,78}		MAMMA3	C ₁₆ PCI	0.9	10.8 ¹⁰¹
	CMC	TTAB	−2.3	5 ²⁰	Kosmella ⁵⁴	DADMAC–NMVA	C ₁₂ PCI	−0.3	2.4 ^{102,103}
	alginate	TTAB	−2.3	13 ⁹⁹		DADMAC–NMVA	C ₁₂ PCI	−0.2	2.2 ^{102,103}
	pectate	TTAB	−2.3	13 ¹⁰⁰		DADMAC–NMVA	C ₁₂ PCI	−0.1	2.1 ^{102,103}
	PAA	TTAB	0.3	1 ¹⁰²		DADMAC	C ₁₂ PCI	−1.5	2.5 ^{31,84}
	DNA	TTAB	−2.3	50 ^{30,78}		PAA	C ₁₂ PCI	0.3	1 ¹⁰²
Mylonas ⁶²	PAM2	SDS	−0.7	1.5 ^{84,104}	Li ^{56,57,60}	DADMAC	SDS	−1.5	2.5 ^{31,84}
	PAM6	SDS	−0.8	2.9 ^{84,104}		AMD2	SDS	−0.9	1.2 ^{30,31,84,102}
	PAM21	SDS	−1.1	8.0 ^{84,104}		AAD	SDS	−0.8	2.0 ^{30,31,84,102}
Kasseh ⁶³	AMPSAM	BDDAB	−2.1	2.7 ^{30,31,84}		AMD1	SDS	−0.8	1.0 ^{30,31,84,102}
	AMPS20AM	BDDAB	−1.9	2.4 ^{30,31,84}		JR400	SDS	−4.2	12 ⁹⁷
Okuzaki ^{52,58,64}	PAMPS	C ₁₂ PCI	−2.2	2.9 ³⁰		DADMAC	SLE ₃ S	−1.5	2.5 ^{31,84}
	PAMPS	C ₈ PCI	−2.2	2.9 ³⁰		AMD2	SLE ₃ S	−0.9	1.2 ^{30,31,84,102}
	PAMPS	C ₁₀ PCI	−2.2	2.9 ³⁰		AAD	SLE ₃ S	−0.8	2.0 ^{30,31,84,102}
	PAMPS	C ₁₂ PCI	−2.2	2.9 ³⁰		AMD1	SLE ₃ S	−0.8	1.0 ^{30,31,84,102}
	PAMPS	C ₁₆ PCI	−2.2	2.9 ³⁰		JR400	SLE ₃ S	−4.2	12 ⁹⁷
	PAMPS	C ₁₈ PCI	−2.2	2.9 ³⁰		DADMAC	SDBS	−1.5	2.5 ^{31,84}
Matullis ⁴⁷	DNA	C ₉ H ₂₁ N	−2.3	50 ^{30,78}		AMD2	SDBS	−0.9	1.2 ^{30,31,84,102}
	DNA	C ₁₀ H ₂₃ N	−2.3	50 ^{30,78}		AAD	SDBS	−0.8	2.0 ^{30,31,84,102}
	DNA	C ₁₁ H ₂₅ N	−2.3	50 ^{30,78}		AMD1	SDBS	−0.8	1.0 ^{30,31,84,102}
	DNA	C ₁₂ H ₂₇ N	−2.3	50 ^{30,78}		JR400	SDBS	−4.2	12 ⁹⁷
	DNA	C ₁₃ H ₂₉ N	−2.3	50 ^{30,78}					

^a $\text{Log}K_{ow}$ values were calculated on the basis of the chemical structure using EPI Suite software: <http://www.epa.gov/opptintr/exposure/pubs/episuitd.htm> ^bThe intrinsic persistence lengths were estimated from the average polymer monomer units or from literature values.

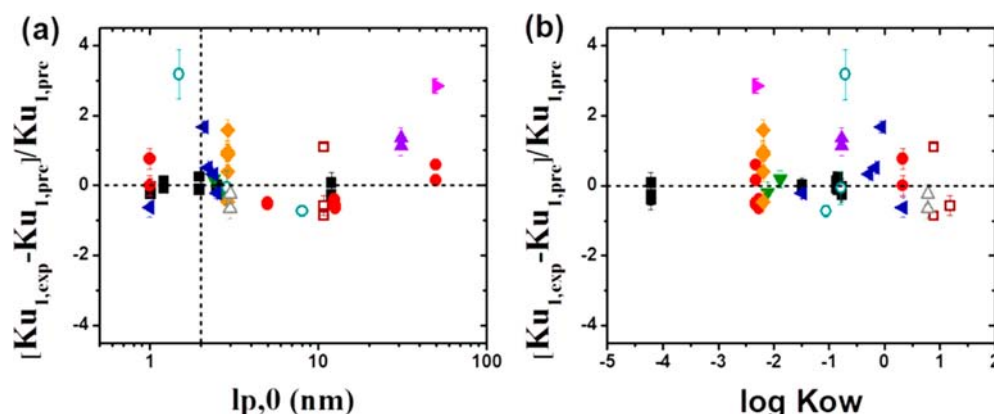


Figure 5. Deviation plots showing the relative error in the binding strength vs (a) the intrinsic persistence length of the PE and (b) PE octanol–water partition coefficient $\text{Log}K_{ow}$ at 25 °C. (black ■) Li; (red ●) Hayakawa; (purple ▲) Liu; (green ▼) Kasseh; (orange ◆) Okuzaki; (blue left-pointing triangles) Kosmella; (pink right-pointing triangles) Matullis; (brown □) Treeby; (light blue ○) Mylonas; (gray △) Lapitsky.

a positive correlation between Ku and a systematic ordering of the aggregate microstructures by performing X-ray and small-angle neutron scattering experiments on a series of PE–surfactant mixtures.⁶⁰ Although specific systems may exhibit properties that reflect these additional parameters, no cross-correlations are evident in the deviation plots. Hence, our choice of independent parameters for correlating the binding strength is valid, and deviations from the correlation are not systematic when viewed globally across the broad range of systems in the literature.

3. CONCLUSION

We have reported a semiempirical relationship for the strength of cooperative binding in oppositely charged, salt-free PE–alkyl surfactant mixtures for a broad range of systems reported in the literature. The cooperative binding strength depends on the surfactant’s hydrophobicity and the PE’s linear charge density. The systems used to define the correlation are very diverse, spanning natural DNA molecules as well as synthetic, industrial-related polymers such as cellulose, hydrogels, and copolymers. Scaling the cooperative binding parameters Ku by the corresponding surfactant micellar free energies leads to a general squared-power dependence on the PE linear charge density. A semiempirical model has been shown to be effective for the estimation of the interaction parameter from the material chemistry. Furthermore, we have shown that this calculation provides a basis for studying additional effects due to other parameters not considered in the correlation, such as PE stiffness and hydrophobicity. This model should be useful for formulating PE–surfactant mixtures and is a promising step toward the rational formulation of such systems to meet specific requirements for the material properties. The practical value of this work is that it provides predictive power to a field that has been dominated by case-by-case studies. This present experimental observation and summary also raises interesting scientific questions concerning the possible dependence of the microstructure of the PSCs formed on the chemistry, which is the subject of ongoing research.

■ ASSOCIATED CONTENT

Supporting Information

List of parameter definitions, derivation of the Ku rescaling law and a summary of the literature data in the Ku master binding

curve. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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