

Electrophoretic NMR characterisation of charged sidechain cationic polyelectrolytes and their interaction with the anionic surfactant, sodium dodecylsulfate

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Keywords

Electrophoretic NMR, surfactant – polymer binding, charge neutralization.

Abstract

Oppositely charged polymers and surfactants show a complex phase behaviour, with large regions of solubility and insolubility dependent on the concentrations of the species present. Here, a series of quaternized hydroxyethyl cellulose (cationic) polymers have been characterised by pulsed-gradient spin-echo NMR (PGSE-NMR) and electrophoretic NMR (eNMR) in simple aqueous (D_2O) solutions and in combination with the oppositely charged (anionic) surfactant, sodium dodecyl sulfate (SDS). Analysis of the effective charge on the polymer derived from both the eNMR and PGSE-NMR results yields a readily interpretable insight into the polymer behaviour – the effective charge on the polymer at infinite dilution shows a linear relationship with the degree of modification.

On addition of low concentrations of SDS, typically $C_{surf} < 5\text{mM}$, the surfactant interacts with the charged polymers, leading to substantial changes in the dynamics of the system (polymer diffusion, viscosity). At these levels of surfactant addition, there is no macroscopic phase separation. Further, the absence of an interaction with the parent, uncharged polymer strongly suggests that the SDS only interacts with the charged moieties present on the functionalized side-groups, and not the polymer backbone. Ultimately, the charge on the soluble polymer/surfactant complex was found to depend linearly on the level of surfactant binding, across a series of polymers with differing levels of modification, with the charge becoming effectively zero at the macroscopic phase separation boundary.

Introduction

NMR methodology – in particular pulsed-gradient spin-echo NMR (PGSE-NMR) – has contributed arguably more than any other technique to the study of polymer / surfactant interactions. PGSE-NMR measures the self-diffusion coefficients of the various species present, and from their absolute and relative magnitudes, structure determining interactions may be quantified. The sister technique of electrophoretic NMR (eNMR) is a relatively new approach, and measures the velocity of charged molecules in the presence of an applied electric field (1–5). The electrophoretic mobility when combined with a knowledge of the diffusion characteristics allows the calculation of the effective charge on the complex. This coupled PGSE-NMR/eNMR approach and has been successfully deployed to study a range of polyelectrolytes in solution - poly(acrylamide) copolymers, poly(styrene sulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC) (6-8), poly(ethylene imine) (9,10) - and mixtures of the non-ionic polymers poly(ethylene oxide) (PEO) (11) and poly(vinyl pyrrolidone) (12) with the anionic surfactant sodium dodecyl sulfate (SDS).

The mechanism of complex formation has previously been explored for both oppositely charged polyions, and oppositely-charged polyelectrolytes with surfactants in the dilute surfactant regime (13–24), involving coacervate formation and site-specific ion-ion interactions. A significant number of parameters are at play including polymer molecular weight, charge density, structure, flexibility, coupled with surfactant molecular architecture and micelle charge density; ultimately, the polymer-surfactant charge ratio is a key factor in coacervate formation (25–34). It is evident in all these studies, that binding between oppositely-charged polymers and surfactants is stronger with higher charge

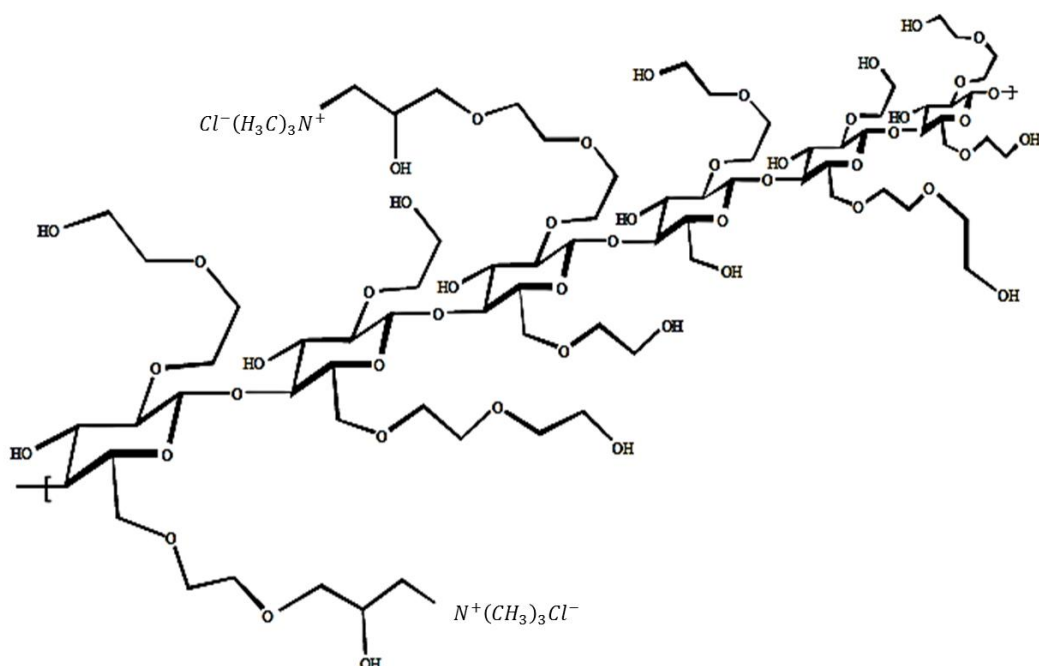
density polymers, but separating the relative importance of the many facets of these systems is complex.

Here, we present a study focussing on one series of polymers of nominally identical molecular weight and structure, with just a minor perturbation being a degree of side-chain modification to introduce charge, to a level of just a few percent.

Experimental

Materials

Quaternized hydroxyethyl cellulose polymers have a cellulosic backbone and may be regarded as polymeric, quaternary ammonium salts of hydroxyethyl cellulose that have been reacted with trimethyl ammonium substituted epoxide, Scheme 1.



Scheme 1 Generic structure of quaternary ammonium salts of hydroxyethyl cellulose polymers (35).

Five different polymers - kindly supplied by Dow Chemical Company with different degrees of modification denoted N (cationic substitution) - have been employed here. These will be referred to by their nominal degree of modification, expressed in terms of the nitrogen content; N=0.5 (\pm 0.1)%, N=0.95 (\pm 0.15)%, N=1.8 (\pm 0.2)%, N =2.7 (\pm 0.2)% along with the parent polymer, N=0%.

Series of polymer and surfactant blends were constructed from stock solutions prepared by first dissolving the appropriate mass of polymer or surfactant in D₂O. Following standing for a few hours to allow the polymer to swell, all stock solutions and samples were rotationally mixed overnight to ensure complete equilibration. The phase behaviour of each system was assessed visually. For the soluble complexes, 0.4ml of each sample was decanted into NMR tubes.

Methods

Experiments were carried out at 25 °C on a 400 MHz Bruker FT NMR spectrometer. In the PGSE-NMR experiment, a stimulated echo sequence was used, in which the diffusion time (Δ) was set to 800 ms, the duration of the gradient pulses (δ) was held constant at 1 ms and their intensity (G) varied from 0.05 - 100 T m⁻¹. Typically, 16-64 scans were accumulated over 32 gradient steps. Self-diffusion coefficients were extracted by fitting the entire dataset *via* CORE modelling based on either 1 or 2 components – as described in the Supplemental Figures 1.1 and 1.2, a stretched exponential as a simple model of a polydisperse polymer, and a single exponential to model the surfactant were found to describe the data rather well. (36,37)

For the electrophoretic NMR experiment, a double stimulated echo sequence was used with constant field gradient parameters, sufficient to partially attenuate the residual water peak, $\delta = 1$ ms, $G = 0.25$ T m⁻¹. In this experiment, the electric field is generated (PL Scientific, Stockholm) by applying 0-200 V across two blackened electrodes touching the solution at the top and bottom of the sample. Gradient and electric field strengths were calibrated by reference to known standards (diffusion – water; electrophoretic mobility – tetramethylammonium bromide) (38).

Results and Discussion

Polymer-only solutions

Figure 1 presents the self-diffusion coefficients of the family of polymers used in this study as functions of concentration and degree of modification in aqueous solution, D₂O. In all cases, with increasing concentration, the self-diffusion coefficient decreases, associated with the increased crowding of the polymers in solution, consistent with the many qualitative descriptors often used in this context, e.g. greater polymer-polymer interactions, increasing phase volumes occupied by the polymer *etc.*

The self-diffusion coefficient is defined as the ratio of the thermal energy ($k_B T$) driving diffusive motion and the friction f opposing that motion, *i.e.* $D_s = \frac{k_B T}{f}$ where k_B is Boltzmann's constant, T is the absolute temperature. Several approaches to fitting the diffusion vs. concentration behaviour exists, but the data presented here fit best to a conventional power series (39) in f ;

$$f = f_0(1 + k_f c + k'_f c^2 \dots). \quad (1)$$

where f_0 is the infinite dilution friction term, k_f and k'_f are molecular weight dependent parameters that define the sensitivity of the concentration dependence of the self-diffusion coefficient to molecular weight. An extrapolation to infinite dilution therefore yields f_0 and thence, D_s^0 , both being defined solely by the hydrodynamic radius of the polymer. From the infinite dilution diffusion coefficients – the dotted black line in figure 1 – it is clear that increasing the charge on the polymer leads to an expansion of the polymer coil due to the repulsion between the charged groups along the polymer backbone.

Across the wider concentration range used in this work, it is likely that these polymers are already starting to overlap and therefore at the higher concentrations any subtle changes in polymer volume (and therefore diffusion coefficient) across the series will be masked by any inherent polydispersity in the molecular weight of the polymer (assuming of course, that the only variable across the series of polymers is the degree of modification). The combined effect of concentration and increasing charge on the polymer results ultimately in a three-dimensional representation with a shallow dependence of the self-diffusion coefficient on degree of modification and a slightly more pronounced dependence on concentration.

The infinite dilution self-diffusion coefficients lead to an (empirical) relationship in terms of the effect of the degree of modification;

$$\frac{D_S^{C=0}(N)}{D_S^{C=0}(N=0)} = N^{-0.48 (+/- 0.04)} \quad (2)$$

Consider now the less established electrophoretic NMR experiment. A typical experimental dataset is presented in Supplemental Figure 2 for an aqueous solution of 1 wt% N=1.6% polymer. The phase of the peaks within the polymer spectra (main image) – effectively, the amount of negative intensity in the peak – vary significantly with increasing electric field strength, but the phase of the water peak is largely invariant. This “phase shift” arises due to the coherent motion of charged species induced by the electric field, but is absent in neutral species (water). The inset figure presents the additional phase shift correction required for those spectra as a function of the electric field. The electrophoretic mobility is linearly proportional to the gradient of this plot, with the sign of the gradient indicating that the polymer is positively charged.

Figure 2 presents the electrophoretic mobilities of the polymers as functions of concentration and degree of modification. The parent polymer shows no electrophoretic mobility, whereas for the modified polymers, the electrophoretic mobility increases with degree of modification at all concentrations. All the electrophoretic mobilities are consistent with cationic charged species. Note that this figure is plotted subtly differently to the diffusion data in figure 1.

Interestingly, the concentration dependence of the electrophoretic mobility is weaker than in the diffusion case, reinforcing the need to consider limiting (infinite dilution) concentration values when interpreting any derived parameters such as charge. Therefore, performing the analogous analysis as in the diffusion study – the friction associated with the electrophoretic mobility of the polymer

follows a polymer series – the electrophoretic mobility can also be extrapolated to infinite dilution, resulting in a second empirical relationship akin to Eqn (2);

$$\frac{\mu^{C=0}(N)}{\mu^{C=0}(N=0)} = N^{+0.43 (+/-0.07)} \quad (3)$$

Interesting, the exponent in both the diffusion and electrophoretic mobility cases is similar, as might be expected if there were a common origin, such as the friction opposing the motion of the polymer.

Finally, noting that at infinite dilution, the charge (q) on the polymer is given by the ratio of the electrophoretic mobility to self-diffusion coefficient scaled by $k_B T$

($z = \frac{\mu k_B T}{D_s e}$) one arrives at an observation that the effective charge on the polymer

at infinite dilution increases largely linearly with degree of modification,

Supplemental figure 3, or from Eqn (3) & (2), $q \propto N^{0.91 +/- 0.07}$. Whilst a linear relationship adequately describes all the data, the N=2.7% sample lies marginally outside a better linear relationship – the dotted line. This might suggest the charge density on the N=2.7% polymer is such that counterion condensation becomes a factor, slightly reducing the prevailing charge. Omitting the N=2.7% datum, increases the exponent by about 10%. We shall return to this point later.

Li *et al* (42) state that for their studies on JR 400 (similar to our N=1.6wt%), assuming a molecular weight of 350,000 g mol⁻¹, JR 400 bears a charge equivalent of 1000 g mol⁻¹, *i.e.* 350e per polymer. The effective charge detected here is 110e, slightly less. In the ensuing sections, eNMR data will therefore be presented as a relative quantity, an approach validated by eNMR data on PAMAM dendrimers, as presented in the Supplemental Section.

Soluble complexes

The interaction between a polyelectrolyte and an oppositely charged ionic surfactant can be characterised by three different interaction zones, usually quantified at fixed polymer concentration with increasing surfactant concentration; a low surfactant concentration, one-phase region consisting soluble complexes that with further addition of surfactant evolve into a two-phase region of coexisting insoluble and soluble complexes, which on further addition of surfactant, leads to a second, one-phase zone (40). Here, we directly determine the prevailing charge on polymer/surfactant complex as the system approaches that phase boundary.

Binding of anionic surfactants to the sort of cationic polyelectrolytes studied here leads to associative phase separation over a broad range of compositions, usually with gel-like concentrated phases rich in both polymer and surfactant (41). Accordingly, to identify the phase boundaries in these systems, the phase behaviour was explored by observing a set of fixed polymer concentration samples for the polymers as a function of increasing surfactant concentration, Supplemental figure 4. Generally speaking, at low SDS concentrations, the polymer/surfactant complex is soluble, becoming insoluble at specific SDS concentrations that are weakly dependent on the degree of modification. With further increases in SDS concentration, the solution becomes one phase again, associated with the formation of soluble polymer/surfactant complexes. It is tempting to delineate these two one phase regions as being characterised by monomer- and subsequently micellar binding of the SDS to the polymer.

High viscosity soluble polymer/surfactant blends were observed, reflecting gel-like structures, illustrated by substantial decreases in the polymer self-diffusion coefficients. Surface tension data studies show that the interaction occurs as low

as tenths of mM SDS, significantly lower than the critical micelle concentration of the pure surfactant (8mM). The theme of this study is to deploy the common approach of using diffusion data to quantify the binding of surfactant to polymer, and to use that benchmark to understand changes in the electrophoretic mobility. Therefore, for brevity, those data and their preliminary analysis/interpretation are presented in the Supplemental section, to allow the reader to follow the data reduction. Supplemental figure 5 presents the diffusion coefficients of the various polymers as a function of SDS concentration, with the concentration data normalised to the maximum SDS concentration range accessible given the phase behaviour data, *i.e.* $x = \frac{C_{SDS}}{C_{SDS}^{phase\ boundary}}$, such that the phase boundary occurs at $x = 1.0$.

Notwithstanding the brevity, a number of striking observations are immediately visible, firstly that there is no change in the polymer diffusion coefficient for the unmodified polymer, $N=0$, implying minimal interaction with SDS. Indeed, there is no change in the SDS diffusion coefficient. For the modified polymers, there are substantial reductions in the self-diffusion coefficient of the polymer, mirrored by significant increases in viscosity of the systems, and that there appears to be a broad relationship between the level of reduction of the diffusion coefficient and the degree of modification. The notable exception is the $N=2.7\%$ polymer. Given these concentrations, it is hypothesised that these significant changes in polymer mobility (diffusion, viscosity) arise due to surfactant-bridging inter-polymer entanglements; the cationic charges nucleate the formation of polymer bound-surfactant aggregates, with multiple polymers associating with each surfactant aggregate. Fluorescent probe and some preliminary neutron scattering studies (Supplemental figures 7 & 8) suggest that these adsorbed surfactant aggregates

are considerably smaller than conventional micelles one might observe in solution.

From a knowledge of the surfactant self-diffusion coefficient in each solution, a two-state mobility model may be deployed to quantify the level of surfactant binding to the polymer, this insight being broadly consistent with the phase behaviour. The N=2.7% polymer is again somewhat different, with *lower* levels of binding shown at each given solution SDS concentration. It is hypothesised therefore that the level of binding is reduced in this case, due to the competing effects of counterion condensation such that the polymer accommodates a smaller number of surfactant aggregates, but further work is required to confirm this suggestion. Nonetheless, this global PGSE-NMR normalisation enables a presentation of the electrophoretic mobility data, expressed in terms of the level of SDS bound to the polymer, Supplemental figure 9.

Clearly, the changes in electrophoretic mobility – both vertically and horizontally across this plot - are determined predominantly by the number of opposing charges in the various systems, with the electrophoretic mobility (i) increasing with degree of modification for all levels of SDS binding, and (ii) decreasing as a function of SDS binding for degrees of modification. The data contract/expand laterally compared to the *initial or solution* SDS concentration due to the slightly different degrees of binding.

The key, final test of the hypothesis that the electrophoretic mobilities are defined by a “titration” of the polymer charge by the surfactant is determinable by the mobility data. Given that the SDS interacts only with the charged groups, at least within this low surfactant concentration region of the phase diagram, and that the electrophoretic mobility is linearly dependent on charge (Supplemental Figure 3), the *change* in electrophoretic mobility of the polymer should be

equivalent to the change in the *charge*, which would in turn, be expected to follow a linear dependence on bound SDS concentration. The maximum charge on each polymer is given by its electrophoretic mobility when $C_{\text{SDS}} = 0$. Knowing that binding of SDS leads to a reduction in the charge, one may define an equivalence for charge as, expressed in % terms:

$$\Delta\mu^{\%} = \frac{\mu_{\text{SDS}=0}^{\text{N}} - \mu_{\text{SDS}}^{\text{N}}}{\mu_{\text{SDS}=0}^{\text{N}}} \quad (5)$$

By definition, when $C_{\text{SDS}} = 0$, $\Delta\mu^{\%} = 0$ whereas at charge neutralization, $\Delta\mu^{\%} = 100$.

All the electrophoretic mobility data thus calculated appear to fall onto such a common master curve, figure 3, which crudely extrapolates to an effective complete neutralisation (80%) of the cationic (polymer) charge by the adsorbed anionic species coincident with the macroscopically observed phase boundary.

Conclusions

Two measurements of the mobility of a series of quaternized hydroxycellulose polymers have been derived from PGSE-NMR and eNMR measurements. The concentration dependence of the electrophoretic mobility is less pronounced than that of the diffusion, but ultimately on extrapolation to infinite dilution yield a linear relationship between charge on the polymer and degree of modification. On addition of the oppositely charged surfactant, SDS, again, a linear relationship was observed between the charge on the polymer / surfactant complex and the level of surfactant binding, irrespective of the degree of modification of the polymer.

This conclusion demonstrates the correlation between polymer / surfactant complex charge and the macroscopic phase separation boundary.

Acknowledgments

The University of Greenwich and Unilever are gratefully thanked for financial assistance, as is the STFC for provision of beamtime (RB1910084).

Figures

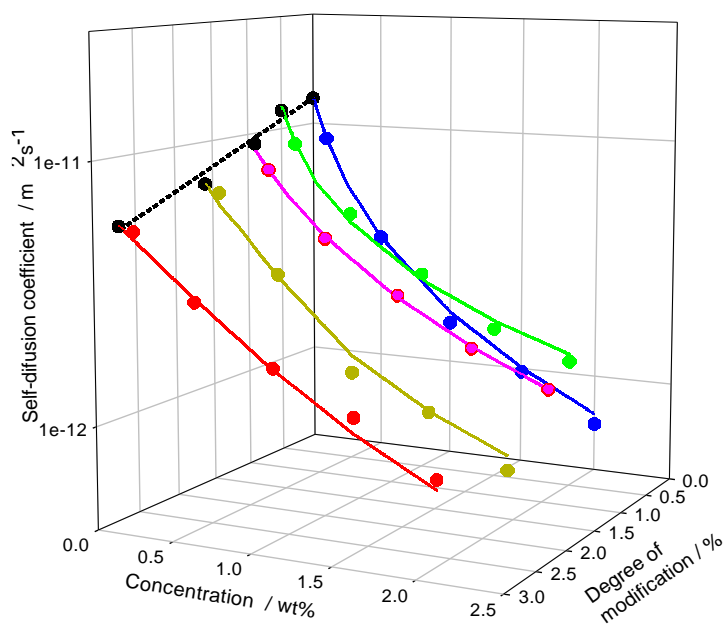


Figure 1 Self-diffusion coefficients of quaternized hydroxycellulose polymers as a function of concentration and degree of modification at 25 °C. The black circles represent the infinite dilution behaviour derived from the concentration analyses described in the text. The dotted line corresponds to an empirical relationship between these infinite dilution diffusion coefficients and the degree of modification.

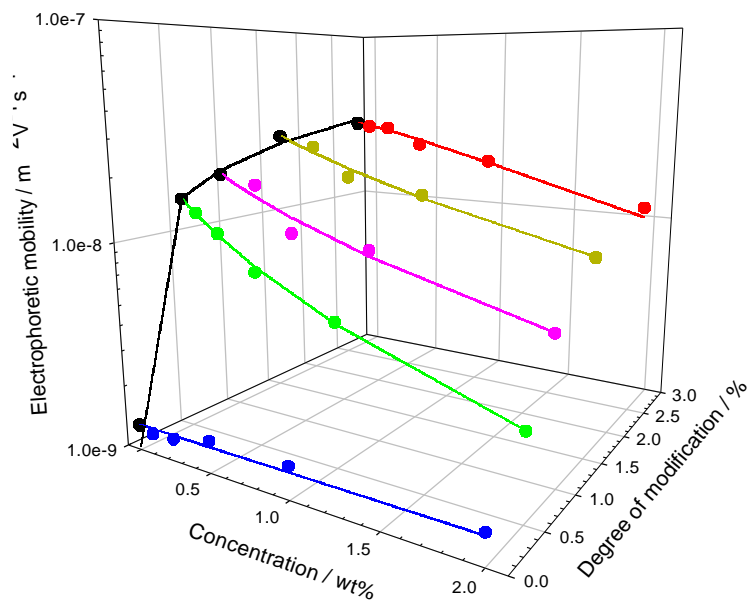


Figure 2 Electrophoretic mobility of quaternized hydroxycellulose polymers as a function of concentration and degree of modification at 25 °C. The black circles represent the infinite dilution behaviour derived from the concentration analyses described in the text. The dotted line corresponds to an empirical relationship between these infinite dilution electrophoretic mobilities and the degree of modification.

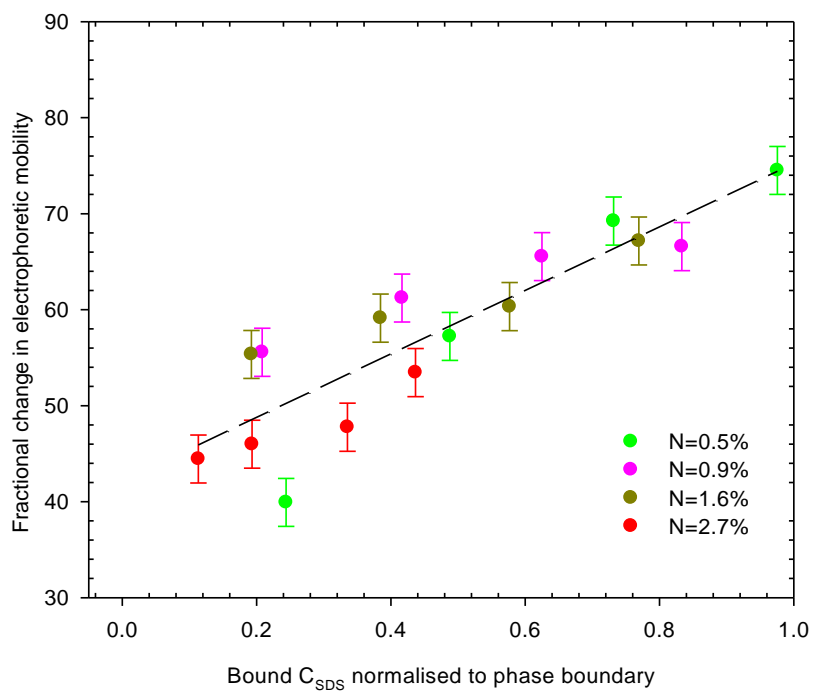


Figure 3 Fractional change (in % terms) on the electrophoretic mobility of the polymer in polymer-SDS blends as a function of bound SDS normalised to the phase boundary, for the series of differing degrees of modification; $C_{\text{polymer}} = 1 \text{ wt } \%$ in D_2O at $25 \text{ }^\circ\text{C}$.

Supporting Information

Analysis of the raw PGSE-NMR and eNMR data to extract the charge on the polymer as a function of binding; its correlation with the phase diagram; preliminary small angle neutron scattering and fluorescence data to frame the discussion on the state of the adsorbed surfactant; related data on PAMAM electrophoresis as calibrant of the eNMR data.

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