Contents lists available at ScienceDirect

Journal of Colloid And Interface Science

journal homepage: www.elsevier.com/locate/jcis

COLLEGE AND SCHOOL AND

Regular Article

Comparing polymer-surfactant complexes to polyelectrolytes

Isaac J. Gresham^{a,1,3}, Edwin C. Johnson^{b,2,3}, Hayden Robertson^b, Joshua D. Willott^b, Grant B. Webber^b, Erica J. Wanless^b, Andrew R.J. Nelson^c, Stuart W. Prescott^{a,*}

^a School of Chemical Engineering, UNSW Sydney, Sydney, 2052, NSW, Australia

^b College of Science, Engineering and Environment, University of Newcastle, Callaghan, 2308, NSW, Australia

° ANSTO, Locked Bag 2001, Kirrawee DC, 2232, NSW, Australia

G R A P H I C A L A B S T R A C T



ARTICLE INFO

Keywords: Poly(N-isopropylacrylamide) Polymer brushes Sodium dodecylsulfate Surfactants Responsive polymers Electrolyte

ABSTRACT

Hypothesis: Understanding the complex interactions between polymers and surfactants is required to optimise commercially relevant systems such as paint, toothpaste and detergent. Neutral polymers complex with surfactants, forming 'pearl necklace' structures that are often conceptualised as pseudo-polyelectrolytes. Here we pose two questions to test the limits of this analogy: Firstly, in the presence of salt, do these polymer-surfactant systems behave like polyelectrolytes? Secondly, do polymer-surfactant complexes resist geometric confinement like polyelectrolytes?

Experiments: We test the limits of the pseudo-polyelectrolyte analogy through studying a poly(*N*-isopropylacrylamide) (PNIPAM) brush in the presence of sodium dodecylsulfate (SDS). Brushes are ideal for interrogating pseudo-polyelectrolytes, as neutral and polyelectrolyte brushes exhibit distinct and well understood behaviours. Spectroscopic ellipsometry, quartz crystal microbalance with dissipation monitoring (QCM-D), and neutron reflectometry (NR) were used to monitor the behaviour and structure of the PNIPAM-SDS system as a function of NaCl concentration. The ability of the PNIPAM-SDS complex to resist geometric confinement was probed with NR.

Findings: At a fixed SDS concentration below the zero-salt CMC, increasing NaCl concentration <100 mM promoted brush swelling due to an increase in osmotic pressure, not dissimilar to a weak polyelectrolyte. At these salt concentrations, the swelling of the brush could be described by a single parameter: the effective

* Corresponding author.

https://doi.org/10.1016/j.jcis.2023.10.101

Received 14 September 2023; Received in revised form 12 October 2023; Accepted 19 October 2023 Available online 23 October 2023

0021-9797/© 2023 The Author(s). Published by Elsevier Inc. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).





E-mail address: s.prescott@unsw.edu.au (S.W. Prescott).

¹ Current address: The School of Chemistry, The University of Sydney, Australia.

² Current address: Department of Chemistry, University of Sheffield, Dainton Building, Brook Hill, Sheffield, S3 7HF, UK.

³ These authors contributed equally.

CMC. However, at high NaCl concentrations (e.g., 500 mM) no brush collapse was observed at all (non-zero) concentrations of SDS studied, contrary to what is seen for many polyelectrolytes. Study of the polymer-surfactant system under confinement revealed that the physical volume of surfactant dominates the structure of the strongly confined system, which further differentiates it from the polyelectrolyte case.

1. Introduction

Mixtures of polymer and surfactant are ubiquitous in many products, where their function is often a direct result of interfacial phenomena, either within the formulation or at the point of application. Therefore, understanding the interaction between these two classes of material at interfaces is of fundamental academic and commercial interest. Throughout this work we compare the behaviour of the polymer-surfactant complexes to polyelectrolytes. Complexes of neutral polymers and surfactants are often described as 'polyelectrolyte-like' [1–6], due to the decoration of the otherwise neutral polymer chain with charged surfactant micelles and its subsequent swelling. We test the limits of this analogy, gaining a better understanding of these important systems and answering the question: to what extent can polymer-surfactant complexes be conceptualised as polyelectrolytes? Herein, we study the behaviour of a polymer-surfactant complex in two systems relevant to their application: varying ionic strength and mechanical confinement.

The behaviour of polyelectrolytes is distinct to that of neutral polymers due to their charged nature; these differences are particularly evident when the local polymer concentration is high or the ionic strength of solution is varied [7]. Surface-tethered or adsorbed polyelectrolytes are of particular interest due to their ability to lubricate interfaces [8,9], stabilise particles [10] and otherwise resist confinement [11]. While polyelectrolyte behaviour is complex, and has been the subject of significant study [7,10,12–15], we focus on three phenomena, specifically for surface-grafted polymer brushes:

- The *salting-in* (of weak polyelectrolytes) at low salt-concentrations (1 to 100 mM) [12,13].
- The *salting-out* (of all polyelectrolytes) at higher salt concentrations (100 to 1000 mM) [12,13].
- The resistance of polyelectrolyte brushes to mechanical confinement [11].

All three phenomena are driven by the osmotic pressure differential between the brush and bulk solvent.

Here we use a model system to study these phenomena: a polymer brush of neutral poly(N-isopropylacrylamide) (PNIPAM), a thermoresponsive polymer with a critical solution temperature (CST) of 32.5 °C in bulk aqueous solution. The experimentally accessible CST of PNIPAM makes it an ideal candidate for examining pseudo-polyelectrolyte behaviour as any increase in polymer stability induced by the surfactant can be easily assessed. As PNIPAM is thermoresponsive, the PNIPAMsurfactant complexes can most readily be compared to a thermoresponsive weak polyelectrolyte like poly[2-(dimethylamino)ethyl methacrylate] (PDMA). The LCST of PDMA (and other tertiary amine methacrylates) is shifted to higher temperatures as the degree of protonation is increased at pH values below the pK_a [16]. Eventually all thermoresponsive behaviour is lost when the polymer is sufficiently protonated. Furthermore, the use of polymer brushes eliminates instability issues associated with untethered studies and allows the polymer to be examined in poor solvent conditions or above the CST. By examining polymer brushes at planar surfaces, we enable use of surface-sensitive techniques such as spectroscopic ellipsometry, quartz crystal microbalance with dissipation monitoring (QCM-D), and neutron reflectometry (NR). We have previously studied the behaviour of our PNIPAM brush system in the presence of several surfactants [17]. The addition of sodium dodecylsulfate (SDS) imbues PNIPAM with charge, exhibiting strong swelling and resisting thermally induced collapse [17].

1.1. Response to ionic strength

To probe the pseudo-polyelectrolyte nature of polymer-surfactant systems, the behaviour of SDS-decorated PNIPAM brushes is examined in the presence of sodium chloride (NaCl). The properties of each of these materials have been well characterised in isolation, and the phenomenological behaviour of each binary system (PNIPAM-NaCl, PNIPAM-SDS, SDS-NaCl) is also well understood. For brevity, a very concise summary of the three binary systems in aqueous conditions is made here with more details provided in the Supporting Information.

- PNIPAM-NaCl. The presence of certain ions, such as chloride, at concentrations ≈100 to 1000 mM results in a reduction in polymer solubility, *decreasing the CST*, and an associated structural collapse due to salting-out effects [18–22].
- **PNIPAM-SDS.** SDS has been shown to adsorb to PNIPAM as complete micelles that are smaller than their free-solution counterparts [23,24], imbuing the polymer with charge and *increasing the CST*. For brushes, when the concentration of SDS was above the critical micelle concentration (CMC), considerable swelling was observed with a complete suppression of temperature response [17].
- **SDS-NaCl.** Increasing NaCl concentration reduces the CMC through micellar charge screening [25,26]. The CMC of SDS is approximately halved from 8 mM in water to 5 mM in 10 mM NaCl.

Only a single study has examined the free solution ternary PNIPAM-SDS-NaCl system. Patel et al. [27] observed that at a given surfactant concentration (2 to 50 mM), increasing the NaCl concentration decreased the cloud point of PNIPAM. However, as these experiments were carried out at a fixed PNIPAM concentration of 1 wt% (\approx 90 mM PNIPAM repeat units), it is likely that these results are influenced by the depletion of surfactant from free solution. Specifically, they plot cloud point against the *added* SDS, whereas the more relevant parameter (from an equilibrium perspective) is the *free* SDS concentration. The ternary system has not been examined in the brush geometry.

1.2. Confinement

We also examine structural changes in geometrically confined PNIPAM-SDS complexes with neutron reflectometry. By examining the PNIPAM brush structure under confinement and comparing it to the behaviour of conventional polyelectrolytes, we gain further insight into the nature of the interactions of the polymer and surfactant, particularly as a mimic of surfaces 'in action' at contacting surfaces.

1.3. Critical parameters for polymer-surfactant systems

There are two critical parameters that describe the polymersurfactant system in this work:

- 1. Critical aggregation concentration (CAC): The *free* surfactant concentration at which surfactant molecules begin to adsorb onto polymer chains.
- 2. Critical micelle concentration (CMC): The *free* surfactant concentration at which free micelles are formed.

In free solution a third parameter, the polymer saturation point (PSP), is needed to account for the depletion of free surfactant from solution due to surfactant-polymer binding. However, in the current system the depletion of free surfactant through polymer adsorption is insignificant due to the vanishingly small concentration of polymer in the system. In short, the *free* surfactant concentration is equal to the *total* surfactant concentration.

Both CAC and CMC are dependent on temperature [28–30] and ionic strength [25,26]. To simplify discussion, we denote two extrinsic CMCs:

- 1. CMC^o: The CMC of the surfactant in pure water at 25 °C (no polymer or salt, for SDS 8.07 mM [28,29,31,32]).
- CMC^{eff}: The effective CMC of the surfactant-NaCl solution (no polymer, Figure S1 [25,26]).

Due to the aforementioned lack of surfactant depletion, we take the CMC of our systems as the CMC^{eff} .

2. Materials and methods

2.1. Materials

Single-side polished silicon blocks (100 mm diameter, 10 mm thick), with a native oxide layer, were used as brush substrates for neutron reflectometry experiments. For ellipsometry experiments appropriately sized substrates were cut from 100 mm diameter, 1 mm thick native oxide silicon wafers. All silicon was purchased from EL-CAT Inc. (USA). QSensor QSX 303 SiO₂-coated QCM-D sensors (Biolin Scientific) were purchased from ATA Scientific and cleaned before use by 30 seconds of plasma treatment followed by washing in 2 wt% aqueous SDS, rinsing with MilliQ water, and drying under nitrogen.

SDS (\geq 98%) and NaCl were purchased from Sigma Aldrich; SDS was recrystallised in ethanol before use. Deuterated SDS (dSDS) was purchased from Cambridge Isotope Laboratories and used as received. Reagents used in the synthesis of the PNIPAM brushes are detailed in the Supporting Information.

2.2. Polymer synthesis

PNIPAM brushes were grafted from silicon wafers via activators regenerated by electron transfer atom transfer radical polymerisation (ARGET-ATRP) [33], as per the protocol of Humphreys et al. [34]; full details of the method are included in the Supporting Information. For NR modelling, brushes are characterised by their interfacial volume (\hat{V}_1), which is the volume of polymer per unit area, with units of length [35]. The dry thicknesses and interfacial volumes of the brushes used in this work are detailed in Table 1.

Table 1

Dry thicknesses of the brush samples used in this work.

In situ	Sample	Substrate	Dry thickness (nm) via		\hat{V}_{I}
technique	number	type	Ellipsometry	NR	(nm)
Ellips.	-	20 mm Si wafer	$150\pm10^{\dagger}$	_	$\approx 135^{\$}$
QCM-D	1	QSensor QSX 303	$\approx 13^{\ddagger}$	_	$\approx 12^{\$}$
QCM-D	2	QSensor QSX 303	$pprox 20^{\ddagger}$	_	$\approx 18^{\S}$
NR	1	100 mm Si block	$30.1 \pm 0.7^{*}$	30.4	25.7
NR	2	100 mm Si block	$17.4 \pm 0.6^{*}$	18.7	15.5
NR	3	100 mm Si block	$16.1 \pm 0.3^{*}$	16.7	13.9

 * Taken from 16 measurements over a 40×40 mm area in the centre of the wafer, see Figure S3. Uncertainty is the standard deviation.

^{*} Approximated from a sibling wafer synthesised in the same reaction mixture. [§] Interfacial volume, \hat{V}_1 , cannot be directly calculated using ellipsometry, values are approximated as 90 % of the dry thickness, according to our previous work [35].

2.3. Ellipsometry

Ellipsometric measurements were performed on an Accurion EP4 ellipsometer using a 1 mL solid-liquid cell. Measurements were performed at an angle of 65°, dictated by the angle of the cell windows, and at 12 wavelengths between 380 and 910 nm inclusive. Measurements were conducted in a series of low-to-high salt concentration sweeps, where each consecutive sweep used a higher surfactant concentration.

The brush studied here is much thicker than those typically studied with ellipsometry [17,36-39], with an interfacial volume of approximately 140 nm. A thicker brush was chosen to increase the sensitivity of ellipsometry to the polymer volume fraction profile; analysis of such diffuse structures has only recently been enabled by developments in modelling software [35,40]. All ellipsometry data were analysed using *refellips* [40], using the freeform model developed for studying brushes described in our previous work [35]. Solvated brush thicknesses were then defined as twice the first moment of the resultant volume fraction profile, based off previous convention [41].

2.4. Quartz crystal microbalance with dissipation, QCM-D

QCM-D studies were performed using a QSense Analyzer (Biolin Scientific) and 5 MHz QSensor QSX 303 SiO₂-coated sensors. In every experiment, all four cells in the QSense analyser were utilised; two cells contained blank silica-coated sensors, while the remaining cells contained silica-coated sensors decorated with 13 and 20 nm PNIPAM brushes, respectively. The cells were connected in parallel and filled with identical solutions, using a peristaltic pump with a rate of 0.3 mL min⁻¹ and a minimum pumped volume of 1.5 mL to each cell. All experiments began in MilliQ water, and were not commenced until all sensor frequencies exhibited less than 0.1 Hz min⁻¹ drift; this typically occurred around an hour after the cells were filled.

QCM-D experiments were performed at a constant temperature (20 °C) as a function of SDS and NaCl concentration. The Δf and ΔD values reported are relative to the frequency and dissipation value of the wafer in pure water and have had the blank QCM-D sensor signals subtracted. This means that the signal is due solely to the interaction of the solution components with the PNIPAM brush, not the solution density, viscosity, ionic strength or interaction with the substrate. An example of the raw data (including the blank sensor signal) is provided in Figure S11. The brush was measured first in salt solutions in the absence of surfactant before performing salt ramps at increasing surfactant concentrations. Salt concentration at a fixed surfactant concentration.

2.5. Neutron reflectometry: PNIPAM, SDS, NaCl

Specular neutron reflectometry measurements were conducted on the *Platypus* reflectometer at the 20 MW OPAL reactor (ANSTO, Sydney) [42]. Measurements were made at angles of 0.6 and 3.2° for dry samples and 0.8 and 3.5° for solvated samples, yielding useful data within *Q*-ranges of 0.0073 to 0.31 Å⁻¹ and 0.0096 to 0.31 Å⁻¹ respectively. Choppers 1 and 4 were used for all experiments, and data reduction was performed using *refnx* [43] following the standard procedure for *Platypus* [42], producing a final resolution of $\Delta Q/Q = 8.8\%$. Solvated experiments were carried out in standard solid–liquid cells (silicon backed) sandwiched between two heat-exchange plates, the temperature of which was controlled by a Julabo FP50-HE heater/chiller unit.

The experiments were performed on sample NR1 (Table 1) in both D_2O and CM solutions. 'CM' refers to a mixture of 19.7 vol% D_2O and 80.3 vol% H_2O , intended to match the SLD of PNIPAM (Table 2). In D_2O -dSDS solutions, contrast between the brush and the solvent is measured while in the CM solutions scattering from dSDS is highlighted.

Hydrogenous surfactant was not used in the unconfined NR experiments as it did not have sufficient contrast with the hydrogenous

 $^{^{\}dagger}$ Taken from 5 points over the wafer surface. Uncertainty is the standard deviation.

Table 2

Tabulated SLD values of materials used.

Compound	SLD, Å ⁻²	Compound	SLD, Å ⁻²
Si	2.07 ^a	PET*	2.57 ^b
SiO ₂	3.47 ^a	SDS	0.28^{b}
H ₂ O	-0.56^{a}	dSDS	6.16 ^b
CM	0.809^{b}	PNIPAM	0.72 ^c
D ₂ O	6.34 ^a	$\mathbf{PNIPAM}^{\dagger}$	1.25 ^c

^{*a*} Taken from literature.

^b Calculated from mass density [supplier provided] and molecular formula.
^c Experimentally derived.

* PET (polyethylene terephthalate) is used as the flexible backing material in the confined NR experiments.

[†] For PNIPAM with a deuterated amide.

PNIPAM. The SLD values used in the current work are collated below. Values determined from the mass density and molecular formula of compounds are indicative only.

Collected NR data were analysed using *refnx* [43]. Polymer volume fraction profiles were modelled with a freeform model [35] utilising the fitting methodology from our previous work [17]. We note that in this more complex system some of the scattering signal in the CM experiments may be due to an accumulation of sodium and chloride ions within the brush, which have an SLD greater than that of the CM solvent. The SLD of these ions is impossible to calculate precisely, as their volume is dependent on their chemical environment. We assume that the non-polymer, non-solvent component (the dSDS NaCl complex, which produces the reflectivity profiles in Fig. 3) has an SLD equivalent to that of dSDS ($6.16 \times 10^{-6} \text{ Å}^{-2}$) and report corresponding volume fraction profiles. Scattering from salt ions will affect the magnitude of these volume fraction profiles, but not their overall shape.

2.6. Neutron reflectometry: PNIPAM, SDS, confinement

The confinement experiments were also performed on the *Platypus* reflectometer, utilising a custom-built sample environment described in our previous publications [44,45]. Briefly, a PNIPAM-decorated 100 mm silicon wafer was placed into the sample environment such that the brush-coated surface was parallel to, and 3 mm away from, a clean polyethylene terephthalate (PET) sheet. The PET sheet was forced against the sample via pneumatic pressure to control the degree of confinement, and the temperature was controlled via a Julabo FP50-HE heater/chiller unit. Measurements were made at angles of -0.35 and -1.5° (i.e. a downwards reflection on *Platypus*), yielding useful data within *Q*-ranges of 0.004 to 0.13 Å^{-1} .

The experiments were performed on sample NR2 and NR3 (Table 1) in both H_2O -hSDS solutions (to enable determination of the silica-PET separation) and in CM-dSDS solutions (to highlight scattering from SDS). Before confinement, the surface was wet with 1 mL of surfactant solution, and the driving pressure increased to 0.1 bar; this slightly deformed the PET sheet, dispersing the solution across the entire sample surface. The system was left in this unconfined state to allow the brush to equilibrate with its solvent environment (over tens of minutes). After equilibration, the PET film was brought into molecular contact with the surface by slowly increasing the pressure. Molecular confinement was confirmed by a critical edge for silicon-PET appearing at Q = 0.0054 Å⁻¹ (Figure S10).

Collected NR data were analysed using *refnx*. H_2O -hSDS was modelled as described previously [44], while CM-dSDS data were analysed using a modified freeform model that allowed for surfactant concentration to be zero close to the substrate, described in the Supporting Information.

3. Results and discussion

We first investigate the effect of NaCl concentration on the swelling behaviour and structure of PNIPAM brush-SDS complexes with ellipsometry, QCM-D, and NR. We then probe the structure and thermoresponse of a PNIPAM brush in the presence of surfactant under geometric confinement. Through contrast variation NR, the distribution of the surfactant molecules throughout the brush is determined in both cases. With these two approaches, we are able to probe the nature of the interactions of the surfactant and polymer to elucidate the mechanism through which neutral thermoresponsive polymers are solubilised by surfactants, and compare this to the behaviour of polyelectrolytes.

3.1. Effect of ionic strength

Before examining the behaviour of SDS-PNIPAM complexes, we briefly summarise the influence of solution ionic strength on polyelectrolyte brush behaviour. The primary consideration when examining polyelectrolytes is the nature of the charged groups; are they strong (permanently charged) or weak (gain charge through acid/base reactions)? At lower salt concentrations (<100 mM), long range electrostatics dictate polyelectrolyte behaviour, allowing weak polyelectrolytes to become charged as electrolyte concentration increases, increasing the osmotic pressure within the brush and causing them to swell (osmotic brush regime). No significant impact on the behaviour of strong polyelectrolytes is observed at these concentrations [12,13]. At high concentrations, for both weak and strong polyelectrolytes, the osmotic pressure difference reverses and brush collapse occurs (salted brush) [12,13].

Naïvely, one might expect the PNIPAM–SDS system to behave as if it were a weak polyelectrolyte [46,47]. In pure water, we expect the PNIPAM-SDS complex would have a charge every 4 to 8 repeat units (charge fraction of 0.125 to 0.25) [17]. This charge fraction is lower than a strong polyelectrolyte in water (e.g., polystyrene sulfonate has a charged fraction of 0.8 [48]). Furthermore, one would expect the charge fraction to be a strong function of ionic strength as in weak polyelectrolytes.

As discussed, the adsorption of SDS to PNIPAM chains increases the LCST of PNIPAM. If this increase in thermal stability is purely electrostatic in nature, as is hypothesised, the influence of NaCl on the PNIPAM-SDS complex should be comparable to a weak polyelectrolyte and its behaviour should be as follows. At a fixed SDS concentration below CMC^{\ominus} , but above the CAC, the addition of salt (<100 mM) should lead to polymer swelling as the CMC^{eff} is lowered (analogous to salting-in). This will in turn lead to an increase in micelle binding to the polymer and thus an increase in the adsorbed material and charge fraction within the brush. Above the CMC^{\ominus} , the addition of salt (<100 mM) will have little effect on PNIPAM, inducing at most some polymer swelling as the size of the tethered micelles increases. If the increased SDS micelle adsorption stabilises PNIPAM brush swelling through purely electrostatic means, then the thermoresponse of the PNIPAM will initially be suppressed due to the reduction in CMC^{eff} . The thermoresponse would be expected to return at higher salt concentrations due to the screening of electrostatic interactions, as observed for pure PNIPAM [49] and classical polyelectrolytes [7,12,13,50-52]. This expected collapse at high NaCl concentrations (>100 mM) would be independent of the surfactant concentration. In the rest of this section, we will use ellipsometry, QCM-D and NR to build up a structural understanding of the NaCl-SDS-PNIPAM brush system (illustrated in Fig. 4) and compare system behaviour to the polyelectrolyte case.

3.1.1. Ellipsometry

The ellipsometry data are summarised in Fig. 1, which plots the swelling ratio (solvated thickness divided by \hat{V}_{I}) against the salt concentration. Here we study two concentrations of SDS, 0.5 and 2 ×CMC^{\circ}, at a range of salt concentrations between 0 and 500 mM (covering 0.5 to 25 ×CMC^{eff}). The volume fraction profiles from which the first moments are derived, as well as the experimental and modelled Δ and Ψ values, are shown in Figure S2.



Fig. 1. Swelling ratios, extracted from the volume fraction profiles in Figure S2, plotted against (a, c, e) NaCl concentration and (b, d, f) surfactant concentration (C_{surf}) relative to the CMC^{eff} (modulated by NaCl, Figure S1) as a function of temperature (top to bottom) and SDS concentration (colours). Swelling ratio is independent of NaCl and SDS concentration at 15 °C, but becomes a strong function of both as temperature is increased. The swelling behaviour of the system appears to be predominantly sensitive to the concentration of SDS relative to the CMC, although the contribution of NaCl appears to increase at high concentrations (i.e., 500 mM). All data are from the brush labelled *Ellips*. in Table 1. (For interpretation of the colours in the figure(s), the reader is referred to the web version of this article.)

The addition of *NaCl in the absence of SDS* ($0.0 \times CMC^{\circ}$) lowers the swelling ratio at 32 °C (Fig. 1c), corresponding to the volume fraction profile transitioning from an extended (Figure S2a) to a collapsed profile (Figure S2q), consistent with a CST reduction of $\approx 5 ^{\circ}C$ [18,49]. Similarly, the addition of *SDS in the absence of NaCl* increases the CST at $0.5 \times CMC^{\circ}$ and suppresses the thermoresponse completely at $2 \times CMC^{\circ}$ (Figure S2a-c) [17].

The addition of *salt to the* $0.5 \times \text{CMC}^{\oplus}$ *system* caused the PNIPAM layer to swell and suppressed the thermoresponse completely at high salt concentrations. The swelling ratio (Fig. 1a, c, e) and structures (Figure S2) became practically indistinguishable from the $2 \times \text{CMC}^{\oplus}$ profiles above NaCl concentrations of 50 mM. The addition of *salt to the* $2 \times \text{CMC}^{\oplus}$ *system* had no discernible effect on the swelling ratio (Fig. 1a, c, e) or volume fraction profile of the system structures (Figure S2) at any temperature.

The swelling ratios observed in the left panel of Fig. 1 are consistent with the system behaviour scaling around the CMC^{eff} of SDS; when plotting the swelling ratio relative to the dimensionless CMC (C_{surf}/CMC^{eff}), the 0.5 and $2 \times CMC^{\oplus}$ curves overlay (Fig. 1b, d, f). As with previous experiments [17], minimal thermoresponse was observed over the investigated temperature range at SDS concentrations above $1 \times CMC^{eff}$. Interestingly, at no point did the addition of NaCl begin to collapse the brush, as would be expected from a classical polyelectrolyte [7,14]. We highlight that there is a noticeable discontinuity at 250 mM salt concentrations at both SDS concentrations studied, we will return to this feature throughout.

3.1.2. QCM-D

The QCM-D results are summarised in Fig. 2. QCM-D measures both the change in frequency, Δf , and change in dissipation, ΔD , at a variety of overtones (harmonic numbers). Δf is sensitive to the mass within the decay length of the acoustic wave generated by the oscillating sen-

sor. ΔD measures the rate at which the layer dissipates kinetic energy to its environment within the decay length; it can be thought of as a measure of stiffness vs softness or elasticity vs viscosity. As the decay length decreases at higher overtones, comparison of overtones enables structural inferences to be drawn for the QCM-D data [53]. QCM-D was only performed at one temperature, corresponding to the swollen system data in Fig. 1a, b. Here the 3rd and 7th overtones are plotted (3rd to 11th were collected, and exhibit the same trend).

The addition of *salt in the absence of surfactant* is consistent with prior work, with NaCl inducing a positive Δf and negative ΔD , indicating a collapsing brush layer [18,34,49]. Similarly, the addition of *surfactant in the absence of added salt* is consistent with prior work, with SDS inducing a negative Δf and positive ΔD , indicating a swelling brush layer [17].

Focusing first on the difference in trends between 0.5 and $2 \times CMC^{\oplus}$ SDS data with increasing NaCl concentration (Fig. 2a, c), there exist two clear regimes: at low salt concentrations (<50 mM) it is clear that changes in Δf and ΔD remain dependent on surfactant concentration, but at higher salt concentrations (>50 mM), when the $C_{\text{surf}} \geq$ CMC^{eff} , behaviour becomes purely dependent on salt content. This trend matches that observed in the ellipsometry data (Fig. 1a, c, e). Similar to the ellipsometry figure, much of the QCM-D results can be explained by the dimensionless CMC, plotted in Fig. 2b, d.

Focusing on the values of Δf and ΔD in Fig. 2b, d, we first see that for SDS concentrations below $1 \times CMC^{eff} \Delta f$ decreases and ΔD increases at all overtones as salt is added, consistent with the brush swelling and becoming more dissipative due to the reduction in CMC^{eff}. Importantly, Δf does not plateau when the concentration of surfactant is above 1×CMC^{eff}, steadily decreasing as the NaCl concentration is increased. This behaviour is distinct from the pure SDS system (open square data points in Fig. 2b, d), where the frequency plateaued at the CMC even with further increases in SDS concentration [17]. A continued reduction in Δf suggests continued brush swelling in the presence of added NaCl. However the ellipsometry data indicated that no layer swelling was observed (Fig. 1), thus decreasing Δf with increasing NaCl concentration indicates that other material such as adsorbed SDS, NaCl, or associated water are being adsorbed within the brush layer. This is corroborated by the dissipation results where above $1 \times \text{CMC}^{\text{eff}}$ (and at NaCl concentrations less than 250 mM) ΔD decreases. Decreasing dissipation typically corresponds to a reduction in brush swelling [54], however, considering the ellipsometry and Δf results, here it most likely corresponds to a stiffening of the brush. This increase in mass within the brush with increasing salt concentration is illustrated in Fig. 4b, d. Interestingly, a notable change in behaviour at 250 mM can be seen in both Δf and ΔD (Fig. 2a, c) matching that observed in the ellipsometry data. It is worth noting the difference in the response of the higher overtones indicates that this swelling is more pronounced at the periphery of the brush. The convergence of the higher overtones at higher salt concentration suggests adsorbed material becomes more evenly dispersed throughout the brush. This implies a transition from a typical parabolic or exponential brush profile to a more uniform 'slab' like structure. To better understand the physicochemical picture at these conditions we turn to neutron reflectometry.

3.1.3. Neutron reflectometry

NR experiments were performed at a fixed concentration of surfactant over a range of temperatures and salt conditions informed by prior QCM-D and ellipsometry measurements. Here, we study the 0.5 ×CMC $^{\circ}$ SDS system at increasing salt concentrations. This is the most interesting surfactant concentration, as it allows us to explore behaviour above and below CMC^{eff}.

Control measurements in both pure D_2O and CM were performed in the absence of salt and surfactant, with results in Figure S7 showing that the PNIPAM brush exhibits the expected thermoresponse and the CM solution matches the PNIPAM SLD well [34,55]. Additional control measurements were carried out at a range of temperatures and NaCl concentrations to characterise the response of the brush to NaCl; these



Fig. 2. (a, b) Frequency and (c, d) dissipation for the 3^{rd} and 7^{th} overtones from a 13 nm PNIPAM brush (QCM-D 1 from Table 1) at 20 °C. Data is plotted as both a function of (a, c) NaCl concentration and (b, d) $\frac{C_{wef}}{CMC^{wff}}$. No-salt SDS concentration series is taken from our prior work [17] (QCM-D 2 from Table 1). All overtones were recorded and follow the same trend; only two were plotted for clarity. Example raw data is plotted in S11.



Fig. 3. Volume fraction profiles for (*left panels*) PNIPAM and (*right panels*) SDS for the PNIPAM-SDS-NaCl system as a function of increasing temperature (top to bottom) and salt concentration (colours). No data was collected from the contrast matched PNIPAM-SDS-NaCl system at 32.5 °C. The corresponding reflectometry data and modelled profiles are inset; reflectometry profiles are vertically offset and scaled by Q^4 for clarity. The SDS concentration is fixed at $0.5 \times CMC^{\circ}$. As NaCl is added to the system, the brush swells and its thermoresponse is suppressed. Added salt appears to increase the amount of SDS in the brush, although it is impossible to differentiate between surfactant in the brush layer and salt in the brush layer due to their SLDs. Sample is *NR 1* from Table 1.

are shown in Figure S8. The addition of NaCl resulted in the brush collapsing at lower temperatures relative to the brush in the absence of salt, most evident above 100 mM, as expected [18,50].

Generally, in the presence of SDS, the overall behaviour of the PNIPAM brush as a function of temperature is consistent with both the ellipsometry (Fig. 1), and QCM-D measurements (Fig. 2) shown above;

that is, the thermoresponse of PNIPAM (characterised by NR in S7) is suppressed. It is worth noting that there is no discernible difference between 100 and 500 mM salt; between these conditions an inconsistency in behaviour was observed in both ellipsometry and QCM-D. NR indicates that this apparent change in behaviour is due to surfactant or salt adsorption, rather than a structural change in the polymer. We interpret this below.

Moving on to the profiles collected from the contrast matched system used to highlight the location of the surfactant, we observe that reflectometry profiles differ significantly from the control measurements (Figure S7), indicating that there is adsorption of surfactant under all conditions. At the zero salt condition, fringes develop as the temperature is increased, indicating that some surfactant remains in the layer upon brush collapse. These fringes do not appear at higher salt concentrations, consistent with the lack of layer collapse observed with the D₂O dataset (and confirmed with ellipsometry, Fig. 1). The shape of the reflectometry profile for 50 and 100 mM NaCl is comparable at all temperatures, indicating similar levels of adsorption at these conditions; the shape of the profile at 500 mM is distinct. This fits with ellipsometry and OCM-D results, which indicated anomalous behaviour at 500 mM. The surfactant volume fraction profiles produced for high salt concentrations are similar in shape to those observed at the 2 ×CMC⁺ SDS condition in our previous work [17], congruent with the system behaviour scaling around CMC^{\odot} . Interestingly, the volume of adsorbed material (integral of the dSDS volume fraction profile) increases markedly at 500 mM, matching the step-change in Δf and ΔD observed via QCM-D.

3.1.4. Effect of NaCl on structure of SDS-PNIPAM system

In light of our findings above and relevant literature, we propose a model for the structure of the PNIPAM-SDS-NaCl system as a function of salt and surfactant concentration, which we present in Fig. 4.

No NaCl: Previous reports have shown that, in the absence of salt, SDS adsorbs to PNIPAM as complete, spherical micelles [23,24] (Fig. 4a, b). These polymer-adsorbed micelles are always smaller than equivalent free-micelles [23,24,57], but vary in size depending on the surfactant concentration — with aggregation numbers varying from ≈ 8 at the CAC (Fig. 4a) to ≈ 22 at the CMC (Fig. 4b) [57]. Above the CMC, no additional surfactant is incorporated into bound micelles [56]. For brushes, the addition of SDS promotes layer swelling and retards the thermoresponse of PNIPAM. This influence is dependent on surfactant concentration between the CAC and the CMC [3,17]. While in solution, SDS only associates with PNIPAM that is solvated (i.e., not collapsed) [58], in the brush geometry it appears that some surfactant can be trapped within the brush interior (Fig. 4a) [17].

NaCl concentration 0-250 mM, $C_{surf} < CMC^{eff}$: For the ternary system examined here, when the total SDS concentration is below the CMC^{eff} (Fig. 4c), the addition of NaCl results in brush swelling and an increase in the CST (transition from Fig. 4c to 4d). Charge screening due to additional salt at the micelle surface reduces the energetic penalty for micelle formation and lowers the CMC^{eff} [25,26,59]; accordingly, more SDS adsorbs to the polymer. Mechanistically, the increased adsorption of SDS occurs through the growth of micelles with increasing salt concentration (Figure S1) [25,26]. Similar behaviour has been observed for PEO-SDS systems, where the addition of NaCl both reduced the SDS concentration required to swell the polymer and increased the swelling magnitude [60].

NaCl concentration 0-250 mM, $C_{SDS} \ge CMC^{eff}$: When the concentration of SDS $\ge CMC^{eff}$ (Fig. 4d), the polymer *conformation* is independent of the total SDS concentration and can be described by the dimensionless CMC (C_{surf}/CMC^{eff}). However, addition of salt does change the amount of surfactant adsorbed within the layer (Fig. 3), and results in a stiffening of the layer (Fig. 2), potentially through micelles 'cross-linking' the polymer.

NaCl concentration 500 mM, $C_{SDS} \ge CMC^{eff}$: At high NaCl concentrations the system remains highly swollen (Fig. 4e). A change in system structure is observed between 250 and 500 mM NaCl by all

Journal of Colloid And Interface Science 655 (2024) 262-272



Fig. 4. Schematic of the PNIPAM-SDS-NaCl system shown above the (purewater) CST of PNIPAM at various salt concentrations. In the no-salt condition, SDS either (b) associates with PNIPAM, swelling it, or (a) does not interact at all [3,56], depending on its concentration relative to the CMC^{\oplus}. (c, d) Moderate ionic strengths promote the growth of micelles, but the conformation of the polymer still scales around the CMC^{\oplus}. (e) Higher ionic strengths further promote micelle growth, and behaviour cannot be explained by the concentration of the surfactant relative to CMC^{\oplus}. At ≈450 mM NaCl we hypothesise that the geometry of the polymer bound micelles transitions from spherical to rod-like.

techniques. Ellipsometry measures an increase in thickness; QCM-D observes a decrease in Δf and increase in ΔD ; and NR indicates a change in surfactant adsorption. NR, however, does not resolve a change in the polymer structure between 100 and 500 mM. As NR is the most sensitive to polymer structure due to contrast-matching of the surfactant and solvent SLD the change observed at 500 mM must be due to an increase in surfactant adsorption and a corresponding change in the optical (ellipsometry) and mechanical (QCM-D) properties of the layer. This change in surfactant adsorption might be explained by a transition from spherical to worm-like micelles; it has been reported that SDS undergoes this transition at a NaCl concentration of 450 mM (Figure S1c) [26,61,62]. Worm-like micelles (WLMs) would explain the increase in adsorption observed (increase in magnitude Δf and change in ellipsometric thickness). The adsorption of intact WLMs to polymers in solution has previously been reported [63-65]. In this instance, entanglement of the polymer chains with (or cross-linking of the polymer chains by) the WLM could give rise to the unique rheological behaviour, explaining the observed increase in dissipation. We show the polymer adsorbing to the surface of worm-like micelles in Fig. 4, consistent with the low-salt interaction mechanism. It is also possible that the polymer could be incorporated into the core of the worm-like micelles.

3.1.5. Comparison to polyelectrolytes

The swelling of polyelectrolyte brushes is dominated by osmotic forces; the degree of brush swelling is determined predominantly by the increased osmotic pressure induced by ion condensation *within* the brush. However, at high salt concentrations, polyelectrolytes should collapse, from the osmotic pressure of the ions *outside* the brush.



Fig. 5. a, b) Diagram of the confined structures derived from NR in the absence and presence $(1.75 \times CMC^{\circ})$ of surfactant, respectively. c) Normalised separation (separation between the substrate and confining layer divided by the interfacial volume [44]) as a function of SDS concentration for the surface confined by 1 bar of stress at 35 °C in H₂O. Data are from *NR 2* in Table 1. Corresponding reflectivity profiles are provided in (d), with the fringe locations indicated by black arrows. (e) Fitted SLD and (f) corresponding reflectivity profiles for the confined system at 35 °C and 1 bar with SDS and dSDS (black and blue lines, respectively). The hydrogenous SDS data and structure is taken from (c). The reflectometry profiles are vertically offset and scaled by Q^4 for clarity.

Below the CMC^{eff} and at intermediate NaCl concentrations, SDS-PNIPAM complexes behave similarly to a weak polyelectrolyte, with NaCl 'salting-in' the complex by promoting polymer-bound charged groups (SDS micelles) and thereby ion condensation within the brush (hence increasing osmotic pressure) [7]. At these low salt concentrations, the SDS-PNIPAM complex can be compared to a thermoresponsive weak polyelectrolyte, such as poly(tertiary amine methacrylates), where the addition of charge suppressed the thermoresponse [16]. Above the CMC^{eff} and at intermediate NaCl concentrations, SDS-PNIPAM complexes behave similarly to a strong polyelectrolyte, with polymer structure being independent of salt concentration.

However, at high salt concentrations (250 and 500 mM) the behaviour of the PNIPAM-SDS complex deviates from that expected from a polyelectrolyte [16], as no salting-out behaviour occurs. We hypothesise that as the salt concentration increases (and with it, micelle size), the prevailing force preventing brush collapse transitions from osmotic pressure to excluded volume effects. the increase surfactant adsorption. This is analogous to the work of Ehtiati et al. [66], who studied the behaviour of poly[2-(dimethylamino)ethyl methacrylate] polymer brushes as their alkyl side-chain length is increased. They find that steric and hydration (i.e., non-electrostatic) effects dominate system behaviour as the side-chain length increases. To further elucidate the role of osmotic and steric forces within surfactant/polymer complexes, we turn from the effects of salt upon the PNIPAM brush to the effect of geometric confinement.

3.2. Effect of SDS on the confined behaviour of a PNIPAM brush

Polyelectrolyte brushes behave differently to neutral brushes when they are placed under geometrical confinement (subjected to a surfacenormal stress), better resisting mechanical confinement [11,55,67]. In the study of Abbott et al. [11], the behaviour of neutral polyethylene oxide (PEO) brushes were compared to charged poly(acrylic acid) (PAA) brushes, with the PAA more swollen under confinement than PEO. Similarly, the reduction of charge in the PAA brushes (via a change in pH) resulted in brushes which were less able to resist confinement. Response to confinement provides another avenue to examine that pseudo-polyelectrolyte nature of the PNIPAM-SDS system. Here we use the same technique as Abbott et al. [11] to probe the behaviour of PNIPAM-SDS complexes under mechanical confinement.

As above, we examine the behaviour of the PNIPAM-SDS systems above and below the CMC, here using surfactant concentrations of $0.6 \times CMC^{\circ}$ and $1.75 \times CMC^{\circ}$. We conduct two types of measurement, one in H₂O/hSDS and one in CM/dSDS. hSDS experiments are sensitive to the separation between the confining PET film and the silica substrate, while dSDS experiments are sensitive to the distribution of the dSDS within the confined layer. The conditions of greatest interest are those where the PNIPAM brush in water is most confined, that is, at high temperatures or high confining stresses. At these conditions, we expect the presence of the SDS to make the most difference to the system structure. We examine the system at 1 bar, 35 °C (low confining stress, high temperature). Measurements at 5 bar, 25 °C (high confining stress, low temperature) were also conducted with similar outcomes; plots are included in Figure S9.

The results from the hydrogenous confinement study are presented in Fig. 5. We use both a modelling approach and a fringe-spacing analysis to determine the separation between the confining PET film and the silica substrate [44]. Thickness is either directly calculated from the fringe spacing, or defined as the mode of the thickness distribution used to model the data. These thickness values are normalised by dividing by the interfacial volume (analogous to the dry thickness of the polymer layer), such that a value of one corresponds to a completely collapsed (zero solvent fraction) layer. Both modelling and fringe-spacing analyses yield similar trends and show clearly that the addition of SDS increases layer thickness. As expected, this increase in thickness is greater at $1.75 \times CMC^{\oplus}$ than it is at $0.6 \times CMC^{\oplus}$. As previously observed, PNIPAM in pure water collapsed almost completely, exhibiting a normalised separation of ≈ 1.1 [44], while the $1.75 \times CMC^{\oplus}$ SDS system exhibited a normalised separation of ≈ 1.5 . Unconfined experiments indicate a volumetric PNIPAM:SDS binding ratio of between 1:0.5 and 1:1 [17,24,57]. In the confined system we observe normalised separations of ≈ 1.5 , dictating a maximum confined volumetric binding ratio of 1:0.5; indicating that there is less SDS in the confined system than in the unconfined system.

To examine the distribution of SDS within the confined layer, we substituted hydrogenous SDS with dSDS. The dSDS has a significantly

higher SLD than any other component in the system (Table 2), therefore, the experiment becomes sensitive to the SDS distribution within the confined layer, rather than the silica-PET separation. The reflectometry profiles for the SDS and dSDS samples are unequivocally distinct, indicating that the concentration of dSDS within the confined layer is substantial (Fig. 5e, f). This stark difference indicates that a significant amount of SDS is trapped inside the brush upon mechanical confinement, as dSDS is clearly modifying the SLD of the layer. A further discussion of the interpretation of the reflectivity profiles in Fig. 5f is made in the Supporting Information.

The modelling shows that the dSDS was enriched near the substrate, with the dSDS concentration dropping in proximity to the confining surface (Fig. 5e). In isolation, the SLD profile would seem to indicate that the PNIPAM-dSDS layer is only 18 nm thick, but the hydrogenous contrast rules out this possibility as a ≈ 26 nm separation is observed there. The uneven (surface-normal) distribution of SDS in the confined region would produce non-uniform SLD profiles (see Table 2 for SLDs) in the hydrogenous system, and thus explains why we cannot accurately model the collected reflectometry profiles at high SDS concentrations (Fig. 5d). However, the modelling of the dSDS shows clearly that the SDS is concentrated within the confined layer and also that the combined interfacial volume of the PNIPAM and SDS leaves little room for water (solvent fraction ≈ 10 % by comparing the $\hat{V_1}$ of polymer and dSDS to the total $\hat{V_1}$ (Fig. 5e).

We observe similar swelling ratios to the PAA study of Abbott et al. [11], with our 'maximally charged' ($1.75 \times CMC^{\circ}$) SDS-PNIPAM complexes exhibiting a swelling ratio of over 1.5 (Fig. 5). However, given that there is little water retained in the brush layer, our results indicate that the primary mechanism through which SDS increases the layer thickness is steric in nature (rather than electrostatic or osmotic, as in classic polyelectrolytes). The steric mechanism operates through excluded-volume interactions between trapped surfactant molecules and the polymer. Conversely, a confined film where electrostatic or osmotic interaction dominated would still contain a considerable amount of water.

It is worth noting that the tightly-packed structure is likely not at equilibrium. Without confinement, when the PNIPAM-SDS system undergoes a thermal collapse (as can occur at low surfactant concentrations) we observe that the SDS is mostly ejected from the brush layer [17]; Chen et al. [3] observe similar behaviour in free-polymer systems. Here, this surfactant is instead trapped by the macroscopic confining barrier. The structure in Fig. 5e provides some insight as to how the SDS gets trapped. The SLD profile pertaining to dSDS shows that the surfactant is concentrated at the base of the brush (Fig. 5b). Interestingly, there does not appear to be an enrichment of the surfactant near the hydrophobic PET interface. One explanation for this is that PETbound surfactant is able to escape from the system upon confinement, whilst polymer-bound surfactant becomes trapped at the base of the brush.

In summary, PNIPAM-SDS systems resist confinement to a greater degree than pure PNIPAM systems, with the brushes maintaining swelling ratios comparable to other polyelectrolytes [11]. However, unlike polyelectrolytes which resist collapse due to electrostatic repulsion and osmotic pressure, we find that the PNIPAM-SDS system resists collapse due to entrapment of the surfactant within the brush thus is unlikely to be stabilised by electrostatics. This tight-packed polymer-surfactant system resists compression due to the excluded volume effects of trapped surfactant molecules.

4. Conclusion

The pseudo-polyelectrolyte character of PNIPAM brush-SDS complexes was investigated with spectroscopic ellipsometry, QCM-D and neutron reflectometry. The changing thermoresponse of the system at varying salinities provides insight into the electrostatic (cf. polyelectrolytes) and steric mechanisms that solubilise PNIPAM brush-SDS complexes. Similarly, the resistance of the polymer-surfactant complex to mechanical confinement was compared to that of a conventional polyelectrolyte. Through these two approaches, we have gained a deeper understanding of the mechanism through which anionic surfactants interact with neutral polymers and tested the validity of conceptualising these complexes as polyelectrolytes.

In the absence of salt, the behaviour of the brush is dependent on the concentration of SDS. Above the CMC^{\oplus} , micelle adsorption along polymer chains promotes brush solvation and partially suppresses the thermoresponse of PNIPAM. Below the $\text{CMC}^{\,\ominus},$ surfactant adsorption into the brush is low and not sufficient to resist thermal collapse [17]. At a fixed SDS concentration below CMC^o, increasing the concentration of NaCl resulted in an increase in the thickness of the PNIPAM brush as detected by all techniques. This behaviour can be fully explained by a reduction in the CMC^{eff}, and is analogous to the salting-in behaviour of weak polyelectrolytes. However, brush collapse was not observed at high NaCl concentrations, contrary to expected behaviour from true polyelectrolyte brushes [7,10,14], thereby demonstrating that PNIPAM-SDS complexes are not purely stabilised through electrostatic interactions. While ellipsometry showed that brush thicknesses plateaued at higher NaCl concentrations, QCM-D Δf results and NR measurements indicated a continual increase in the adsorbed mass of surfactant within the layer. This SDS adsorption is due to continued charge screening due to additional salt, promoting the adsorption of SDS to the polymer. Additionally, changes in the dissipation at salt concentrations ≥450 mM likely indicate a transition from spherical micelles to worm-like structures. This transition could be further studied in the bulk through diffusion nuclear magnetic resonance or small angle scattering techniques.

PNIPAM-SDS complexes were able to resist collapse in response to applied surface pressure to a greater extent than PNIPAM brushes in the absence of SDS [44]. The swelling ratios of the PNIPAM-SDS complexes were comparable to those observed for polyelectrolyte brushes [11]. Upon confinement, PNIPAM brushes trap a large amount of surfactant in their interior. Excluded volume interactions from the SDS micelles trapped in this non-equilibrium structure are responsible for the brush's resistance to confinement, rather than electrostatic repulsion and high osmotic pressure.

The application of multiple techniques allowed us to interrogate the mechanism through which SDS imparts its stabilising effect on PNIPAM brushes. While the phenomenological behaviour of PNIPAM-SDS complexes is largely reflective of polyelectrolytes, a lack of salting-out behaviour at high salinity and steric factors being the major contributor to brush swelling and resistance to confinement distinguish the two types of systems.

CRediT authorship contribution statement

Isaac J. Gresham: Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. Edwin C. Johnson: Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. Hayden Robertson: Investigation, Writing – review & editing. Joshua D. Willott: Conceptualization, Investigation, Writing – review & editing. Grant B. Webber: Funding acquisition, Resources, Supervision, Writing – review & editing. Erica J. Wanless: Funding acquisition, Resources, Supervision, Writing – review & editing. Andrew R.J. Nelson: Funding acquisition, Methodology, Resources, Software, Supervision, Writing – review & editing. Stuart W. Prescott: Conceptualization, Funding acquisition, Methodology, Resources, Software, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Isaac Gresham, Edwin Johnson, Hayden Robertson, Joshua Willott report financial support was provided by AINSE Ltd. Isaac Gresham, Edwin Johnson, Hayden Robertson report financial support was provided by Australian Government.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by ANSTO through an Australian Centre for Neutron Scattering Program Grant (PP4274). IJG, ECJ, and HR thank the Australian Government and AINSE Ltd. for providing financial assistance for the period when this work was completed (Research Training Program Scholarship and PGRA Award, respectively). JDW thanks AINSE Ltd. for financial assistance from the Early Career Researcher Grant.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.jcis.2023.10.101.

References

- P.W. Zhu, Effects of sodium dodecyl sulfate on structures of poly(*N*isopropylacrylamide) at the particle surface, J. Phys. Chem. B 119 (2015) 359–371, https://doi.org/10.1021/jp510350w.
- [2] P.W. Zhu, L. Chen, Synergistic effects of bound micelles and temperature on the flexibility of thermoresponsive polymer brushes, J. Phys. Chem. B 120 (2016) 11595–11606, https://doi.org/10.1021/acs.jpcb.6b08696.
- [3] J. Chen, H. Xue, Y. Yao, H. Yang, A. Li, M. Xu, Q. Chen, R. Cheng, Effect of surfactant concentration on the complex structure of poly(*N*-isopropylacrylamide)/sodium *n*-dodecyl sulfate in aqueous solutions, Macromolecules 45 (2012) 5524–5529, https://doi.org/10.1021/ma301003r.
- [4] Q. Chen, E.S. Kooij, X. Sui, C.J. Padberg, M.A. Hempenius, P.M. Schön, G.J. Vancso, Collapse from the top: brushes of poly(*N*-isopropylacrylamide) in co-nonsolvent mixtures, Soft Matter 10 (2014) 3134–3142, https://doi.org/10.1039/c4sm00195h.
- [5] B. Cabane, Structure of some polymer-detergent aggregates in water, J. Phys. Chem. 81 (1977) 1639–1645, https://doi.org/10.1021/j100532a008.
- [6] K. Shirahama, K. Tsujii, T. Takagi, Free-boundary electrophoresis of sodium dodecyl sulfate–protein polypeptide complexes with special reference to SDS– polyacrylamide gel electrophoresis, J. Biochem. 75 (1974) 309–319, https://doi. org/10.1093/oxfordjournals.jbchem.a130398.
- [7] J.D. Willott, T.J. Murdoch, G.B. Webber, E.J. Wanless, Physicochemical behaviour of cationic polyelectrolyte brushes, Prog. Polym. Sci. 64 (2016) 52–75, https://doi. org/10.1016/j.progpolymsci.2016.09.010.
- [8] G.W. Greene, L.L. Martin, R.F. Tabor, A. Michalczyk, L.M. Ackland, R. Horn, Lubricin: a versatile, biological anti-adhesive with properties comparable to polyethylene glycol, Biomaterials 53 (2015) 127–136, https://doi.org/10.1016/j. biomaterials.2015.02.086.
- [9] G.W. Greene, R. Thapa, S.A. Holt, X. Wang, C.J. Garvey, R.F. Tabor, Structure and property changes in self-assembled lubricin layers induced by calcium ion interactions, Langmuir 33 (2017) 2559–2570, https://doi.org/10.1021/acs.langmuir. 6b03992.
- [10] J. Rühe, M. Ballauff, M. Biesalski, P. Dziezok, F. Gröhn, D. Johannsmann, N. Houbenov, N. Hugenberg, R. Konradi, S. Minko, M. Motornov, R.R. Netz, M. Schmidt, C. Seidel, M. Stamm, T. Stephan, D. Usov, H. Zhang, Polyelectrolyte Brushes, Springer Berlin Heidelberg, 2004.
- [11] S.B. Abbott, W.M. de Vos, L.L.E. Mears, B. Cattoz, M.W.A. Skoda, R. Barker, R.M. Richardson, S.W. Prescott, Is osmotic pressure relevant in the mechanical confinement of a polymer brush?, Macromolecules 48 (2015) 2224–2234, https://doi.org/10.1021/ma502246r.
- [12] R. Israels, F.A.M. Leermakers, G.J. Fleer, On the theory of grafted weak polyacids, Macromolecules 27 (2002) 3087–3093, https://doi.org/10.1021/ma00089a028.
- [13] R. Israels, F.A.M. Leermakers, G.J. Fleer, E.B. Zhulina, Charged polymeric brushes: structure and scaling relations, Macromolecules 27 (1994) 3249–3261, https://doi. org/10.1021/ma00090a018.
- [14] M. Geoghegan, Weak polyelectrolyte brushes, Soft Matter 18 (2022) 2500–2511, https://doi.org/10.1039/d2sm00005a.
- [15] H. Zhao, C. Wang, Polymer brush-based nanostructures: from surface self-assembly to surface co-assembly, Soft Matter 18 (2022) 5138–5152, https://doi.org/10.1039/ d2sm00458e.

- [16] T. Thavanesan, C. Herbert, F.A. Plamper, Insight in the phase separation peculiarities of poly(dialkylaminoethyl methacrylate)s, Langmuir 30 (2014) 5609–5619, https://doi.org/10.1021/la5007583.
- [17] I.J. Gresham, J.D. Willott, E.C. Johnson, P. Li, G.B. Webber, E.J. Wanless, A.R.J. Nelson, S.W. Prescott, Effect of surfactants on the thermoresponse of PNIPAM investigated in the brush geometry, J. Colloid Interface Sci. 631 (2023) 260–271, https:// doi.org/10.1016/j.jcis.2022.10.071.
- [18] Y. Zhang, S. Furyk, D.E. Bergbreiter, P.S. Cremer, Specific ion effects on the water solubility of macromolecules: PNIPAM and the Hofmeister series, J. Am. Chem. Soc. 127 (2005) 14505–14510, https://doi.org/10.1021/ja0546424.
- [19] M. Biesalski, D. Johannsmann, J. Rühe, Electrolyte-induced collapse of a polyelectrolyte brush, J. Chem. Phys. 120 (2004) 8807–8814, https://doi.org/10.1063/1. 1690242.
- [20] Y. Mir, P. Auroy, L. Auvray, Density profile of polyelectrolyte brushes, Phys. Rev. Lett. 75 (1995) 2863–2866, https://doi.org/10.1103/PhysRevLett.75.2863.
- [21] B.A. Humphreys, E.C. Johnson, E.J. Wanless, G.B. Webber, Poly(*N*isopropylacrylamide) response to salt concentration and anion identity: a brush-on-brush study, Langmuir 35 (2019) 10818–10830, https:// doi.org/10.1021/acs.langmuir.9b00695.
- [22] S.Z. Moghaddam, E. Thormann, The Hofmeister series: specific ion effects in aqueous polymer solutions, J. Colloid Interface Sci. 555 (2019) 615–635, https:// doi.org/10.1016/J.JCIS.2019.07.067.
- [23] L.-T. Lee, B. Cabane, Effects of surfactants on thermally collapsed poly(*N*isopropylacrylamide) macromolecules, Macromolecules 30 (1997) 6559–6566, https://doi.org/10.1021/ma9704469.
- [24] S.J. Mears, Y. Deng, T. Cosgrove, R. Pelton, Structure of sodium dodecyl sulfate bound to a poly(NIPAM) microgel particle, Langmuir 13 (1997) 1901–1906, https:// doi.org/10.1021/la960515x.
- [25] E. Dutkiewicz, A. Jakubowska, Effect of electrolytes on the physicochemical behaviour of sodium dodecyl sulphate micelles, Colloid Polym. Sci. 280 (2002) 1009–1014, https://doi.org/10.1007/s00396-002-0723-y.
- [26] B. Naskar, A. Dey, S.P. Moulik, Counter-ion effect on micellization of ionic surfactants: a comprehensive understanding with two representatives, sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB), J. Surfactants Deterg. 16 (2013) 785–794, https://doi.org/10.1007/s11743-013-1449-1.
- [27] T. Patel, G. Ghosh, S.-i. Yusa, P. Bahadur, Solution behavior of poly(*N*-isopropylacrylamide) in water: effect of additives, J. Dispers. Sci. Technol. 32 (2011) 1111–1118, https://doi.org/10.1080/01932691.2010.497701.
- [28] J.P. Marcolongo, M. Mirenda, Thermodynamics of sodium dodecyl sulfate (SDS) micellization: an undergraduate laboratory experiment, J. Chem. Educ. 88 (2011) 629–633, https://doi.org/10.1021/ed900019u.
- [29] S. Shah, N. Jamroz, Q. Sharif, Micellization parameters and electrostatic interactions in micellar solution of sodium dodecyl sulfate (SDS) at different temperatures, Colloids Surf. A 178 (2001) 199–206, https://doi.org/10.1016/S0927-7757(00)00697-X.
- [30] S.A. Markarian, L.R. Harutyunyan, R.S. Harutyunyan, The properties of mixtures of sodium dodecylsulfate and diethylsulfoxide in water, J. Solution Chem. 34 (2005) 361–368, https://doi.org/10.1007/s10953-005-3056-x.
- [31] A. Cifuentes, J.L. Bernal, J.C. Diez-Masa, Determination of critical micelle concentration values using capillary electrophoresis instrumentation, Anal. Chem. 69 (1997) 4271–4274, https://doi.org/10.1021/ac970696n.
- [32] E. Fegyver, R. Mészáros, The impact of nonionic surfactant additives on the nonequilibrium association between oppositely charged polyelectrolytes and ionic surfactants, Soft Matter 10 (2014) 1953–1962, https://doi.org/10.1039/c3sm52889h.
- [33] K. Matyjaszewski, D. Hongchen, W. Jakubowski, J. Pietrasik, A. Kusumo, Grafting from surfaces for "everyone": ARGET ATRP in the presence of air, Langmuir 23 (2007) 4528–4531, https://doi.org/10.1021/la063402e.
- [34] B.A. Humphreys, J.D. Willott, T.J. Murdoch, G.B. Webber, E.J. Wanless, Specific ion modulated thermoresponse of poly(*N*-isopropylacrylamide) brushes, Phys. Chem. Chem. Phys. 18 (2016) 6037–6046, https://doi.org/10.1039/C5CP07468A.
- [35] I.J. Gresham, T.J. Murdoch, E.C. Johnson, H. Robertson, G.B. Webber, E.J. Wanless, S.W. Prescott, A.R.J. Nelson, Quantifying the robustness of the neutron reflectometry technique for structural characterization of polymer brushes, J. Appl. Crystallogr. 54 (2021) 739–750, https://doi.org/10.1107/s160057672100251x.
- [36] T.J. Murdoch, B.A. Humphreys, E.C. Johnson, G.B. Webber, E.J. Wanless, Specific ion effects on thermoresponsive polymer brushes: comparison to other architectures, J. Colloid Interface Sci. 526 (2018) 429–450, https://doi.org/10.1016/j.jcis.2018. 04.086.
- [37] E.S. Kooij, X. Sui, M.A. Hempenius, H.J.W. Zandvliet, G.J. Vancso, Probing the thermal collapse of poly(*N*-isopropylacrylamide) grafts by quantitative in situ ellipsometry, J. Phys. Chem. B 116 (2012) 9261–9268, https://doi.org/10.1021/jp304364m.
- [38] T.J. Murdoch, J.D. Willott, W.M. de Vos, A. Nelson, S.W. Prescott, E.J. Wanless, G.B. Webber, Influence of anion hydrophilicity on the conformation of a hydrophobic weak polyelectrolyte brush, Macromolecules 49 (2016) 9605–9617, https://doi.org/ 10.1021/acs.macromol.6b01897.
- [39] S. Adam, M. Koenig, K.B. Rodenhausen, K.J. Eichhorn, U. Oertel, M. Schubert, M. Stamm, P. Uhlmann, Quartz crystal microbalance with coupled spectroscopic ellipsometry-study of temperature-responsive polymer brush systems, Appl. Surf. Sci. 421 (2017) 843–851, https://doi.org/10.1016/J.APSUSC.2017.02.078.

- [40] H. Robertson, I.J. Gresham, S.W. Prescott, G.B. Webber, E.J. Wanless, A. Nelson, refellips: a python package for the analysis of variable angle spectroscopic ellipsometry data, SoftwareX 20 (2022) 101225, https://doi.org/10.1016/j.softx.2022. 101225.
- [41] T.J. Murdoch, B.A. Humphreys, J.D. Willott, S.W. Prescott, A. Nelson, G.B. Webber, E.J. Wanless, Enhanced specific ion effects in ethylene glycol-based thermoresponsive polymer brushes, J. Colloid Interface Sci. 490 (2017) 869–878, https:// doi.org/10.1016/j.jcis.2016.11.044.
- [42] M. James, A. Nelson, S. Holt, T. Saerbeck, W. Hamilton, F. Klose, The multipurpose time-of-flight neutron reflectometer "Platypus" at Australia's OPAL reactor, Nucl. Instrum. Methods Phys. Res. B 632 (2011) 112–123, https://doi.org/10.1016/j.nima. 2010.12.075.
- [43] A.R.J. Nelson, S.W. Prescott, refnx: neutron and X-ray reflectometry analysis in Python, J. Appl. Crystallogr. 52 (2019) 193–200, https://doi.org/10.1107/ S1600576718017296.
- [44] I.J. Gresham, B.A. Humphreys, J.D. Willott, E.C. Johnson, T.J. Murdoch, G.B. Webber, E.J. Wanless, A.R.J. Nelson, S.W. Prescott, Geometrical confinement modulates the thermoresponse of a poly(*N*-isopropylacrylamide) brush, Macromolecules 54 (2021) 2541–2550, https://doi.org/10.1021/acs.macromol.0c02775.
- [45] W.M. de Vos, L.L.E. Mears, R.M. Richardson, T. Cosgrove, R.M. Dalgliesh, S.W. Prescott, Measuring the structure of thin soft matter films under confinement: a surface-force type apparatus for neutron reflection, based on a flexible membrane approach, Rev. Sci. Instrum. 83 (2012) 113903, https://doi.org/10.1063/1. 4767238.
- [46] H.G. Schild, D.A. Tirrell, Interaction of poly(N-isopropylacrylamide) with sodium n-alkyl sulfates in aqueous solution, Langmuir 7 (1991) 665–671, https://doi.org/ 10.1021/la00052a013.
- [47] H. Schild, Poly(N-isopropylacrylamide): experiment, theory and application, Prog. Polym. Sci. 17 (1992) 163–249, https://doi.org/10.1016/0079-6700(92)90023-R.
- [48] M. Raposo, J.M. Lourenço, A.M. Botelho do Rego, A.M. Ferraria, P.A. Ribeiro, Counterions — a new approach to control the degree of ionization of polyelectrolytes in layer-by-layer films, Colloids Surf. A 412 (2012) 1–10, https://doi.org/10.1016/j. colsurfa.2012.05.005.
- [49] B.A. Humphreys, E.J. Wanless, G.B. Webber, Effect of ionic strength and salt identity on poly(*N*-isopropylacrylamide) brush modified colloidal silica particles, J. Colloid Interface Sci. 516 (2018) 153–161, https://doi.org/10.1016/j.jcis.2018.01.058.
- [50] K.P. Gregory, G.R. Elliott, H. Robertson, A. Kumar, E.J. Wanless, G.B. Webber, V.S.J. Craig, G.G. Andersson, A.J. Page, Understanding specific ion effects and the Hofmeister series, Phys. Chem. Chem. Phys. 24 (2022) 12682–12718, https:// doi.org/10.1039/D2CP00847E.
- [51] E.B. Zhulina, O.V. Borisov, Poisson-Boltzmann theory of pH-sensitive (annealing) polyelectrolyte brush, Langmuir 27 (2011) 10615–10633, https://doi.org/10.1021/ la201456a.
- [52] I.E. Dunlop, R.K. Thomas, S. Titmus, V. Osborne, S. Edmondson, W.T. Huck, J. Klein, Structure and collapse of a surface-grown strong polyelectrolyte brush on sapphire, Langmuir 28 (2012) 3187–3193, https://doi.org/10.1021/la204655h.
- [53] K. Ehtiati, S.Z. Moghaddam, A.E. Daugaard, E. Thormann, How dissociation of carboxylic acid groups in a weak polyelectrolyte brush depend on their distance from the substrate, Langmuir 36 (2020) 2339–2348, https://doi.org/10.1021/acs. langmuir.9b03537.

- [54] J.D. Willott, T.J. Murdoch, B.A. Humphreys, S. Edmondson, E.J. Wanless, G.B. Webber, Anion-specific effects on the behavior of pH-sensitive polybasic brushes, Langmuir 31 (2015) 3707–3717, https://doi.org/10.1021/acs.langmuir.5b00116.
- [55] T.J. Murdoch, B.A. Humphreys, J.D. Willott, K.P. Gregory, S.W. Prescott, A. Nelson, E.J. Wanless, G.B. Webber, Specific anion effects on the internal structure of a poly(*N*-isopropylacrylamide) brush, Macromolecules 49 (2016) 6050–6060, https:// doi.org/10.1021/acs.macromol.6b01001.
- [56] J. Chen, X. Gong, H. Yang, Y. Yao, M. Xu, Q. Chen, R. Cheng, NMR study on the effects of sodium n-dodecyl sulfate on the coil-to-globule transition of poly(Nisopropylacrylamide) in aqueous solutions, Macromolecules 44 (2011) 6227–6231, https://doi.org/10.1021/ma201269u.
- [57] Y. Mylonas, G. Staikos, P. Lianos, Investigation of the poly(N-isopropylacrylamide)sodium dodecyl sulfate complexation with viscosity, dialysis, and time-resolved fluorescence-quenching measurements, Langmuir 15 (1999) 7172–7175, https:// doi.org/10.1021/la9901550.
- [58] J. Chen, J. Spěváček, L. Hanyková, NMR methods to study effects of additives on phase separation of thermoresponsive polymer, Macromol. Symp. 339 (2014) 24–32, https://doi.org/10.1002/masy.201300130.
- [59] E.J. Wanless, W.A. Ducker, Organization of sodium dodecyl sulfate at the graphitesolution interface, J. Phys. Chem. 100 (1996) 3207–3214, https://doi.org/10.1021/ jp952439x.
- [60] Y. Masuda, K. Hirabayashi, K. Sakuma, T. Nakanishi, Swelling of poly(ethylene oxide) gel in aqueous solutions of sodium dodecyl sulfate with added sodium chloride, Colloid Polym. Sci. 280 (2002) 490–494, https://doi.org/10.1007/s00396-001-0636-1.
- [61] S. Hayashi, S. Ikeda, Micelle size and shape of sodium dodecyl sulfate in concentrated NaCl solutions, J. Phys. Chem. 84 (1980) 744–751, https://doi.org/10.1021/ j100444a011.
- [62] M. Almgren, J.C. Gimel, K. Wang, G. Karlsson, K. Edwards, W. Brown, K. Mortensen, SDS micelles at high ionic strength. A light scattering, neutron scattering, fluorescence quenching, and cryoTEM investigation, J. Colloid Interface Sci. 202 (1998) 222–231, https://doi.org/10.1006/jcis.1998.5503.
- [63] I. Couillet, T. Hughes, G. Maitland, F. Candau, Synergistic effects in aqueous solutions of mixed wormlike micelles and hydrophobically modified polymers, Macromolecules 38 (2005) 5271–5282, https://doi.org/10.1021/ma0501592.
- [64] J.A. Shashkina, O.E. Philippova, Y.D. Zaroslov, A.R. Khokhlov, T.A. Pryakhina, I.V. Blagodatskikh, Rheology of viscoelastic solutions of cationic surfactant. Effect of added associating polymer, Langmuir 21 (2005) 1524–1530, https://doi.org/10. 1021/la0482756.
- [65] E.K. Penott-Chang, L. Gouveia, I.J. Fernández, A.J. Müller, A. Díaz-Barrios, A.E. Sáez, Rheology of aqueous solutions of hydrophobically modified polyacrylamides and surfactants, Colloids Surf. A 295 (2007) 99–106, https://doi.org/10.1016/J. COLSURFA.2006.08.038.
- [66] K. Ehtiati, S.Z. Moghaddam, A.E. Daugaard, E. Thormann, Crucial nonelectrostatic effects on polyelectrolyte brush behavior, Macromolecules 54 (2021) 3388–3394, https://doi.org/10.1021/acs.macromol.0c02526.
- [67] J.D. Willott, T.J. Murdoch, G.B. Webber, E.J. Wanless, Nature of the specific anion response of a hydrophobic weak polyelectrolyte brush revealed by AFM force measurements, Macromolecules 49 (2016) 2327–2338, https://doi.org/10.1021/ acs.macromol.5b02656.