Andersson Trojer, M., Eastoe, J., & Mohamed, A. (2013). A highly hydrophobic anionic surfactant at oil-water, water-polymer and oil-polymer interfaces: Implications for spreading coefficients, polymer interactions and microencapsulation via internal phase separation. *Colloids and Surfaces A. Physicochemical and Engineering Aspects*, 436, 1048-1059. <https://doi.org/10.1016/j.colsurfa.2013.08.005>

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[10.1016/j.colsurfa.2013.08.005](https://doi.org/10.1016/j.colsurfa.2013.08.005)

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A highly hydrophobic anionic surfactant at the oil-water, water-polymer and oil-polymer interfaces: Implications on spreading coefficients, polymer interactions and microencapsulation *via* internal phase separation

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Abstract

Multicore-shell particles consisting of a poly(methyl methacrylate) shell and dodecane cores have been prepared *via* the internal phase separation method using the oil-soluble dispersant sodium 1,5-dioxo-1,5-bis(3,5,5-trimethylhexyloxy)-3-((3,5,5 trimethylhexyloxy)carbonyl)pentane-2-sulfonate (TC4) and the water-soluble dispersant poly(diallyldimethylammonium chloride) (PDADMAC) in combination. The multicore-shell particles have been investigated using SEM, light microscopy and microelectrophoresis. The detailed influence of TC4 on the oil-water, water-polymer and oil-polymer interfaces and its interaction with PDADMAC have been investigated using quartz crystal microbalance with dissipation monitoring (QCM-D) and different optical tensiometry methods. TC4 stabilises in particular the polymer-water interface in the presence of PDADMAC instead of the oil-water interface in contrast to water-soluble surfactants. In addition, the oil-polymer interface is stabilised by TC4 which prevents coalescence of the oil droplets and leads to multicore-shell morphology rather than single core-shell.

Keywords

Microcapsule, Dilatational rheology, Negative interfacial free energy, Lewis acid-base, Langmuir adsorption, Surface free energy

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1 Introduction

Hydrophobic surfactants are used in a variety of applications spanning from solubilisation of actives in micelles or mesophases and heterogeneous catalysis to lubrication of surfaces[1]. A proper control of surfactants' interfacial activity is of paramount importance for their successful implementation. Recently, Mohamed and Eastoe have designed, synthesised and investigated highly hydrophobic anionic surfactants for use as CO₂-water emulsifier[2]. The use of supercritical CO₂ as solvent is a promising approach to cut CO₂-emissions[2, 3]. However, CO₂ is a weak non-polar solvent. Yet, the solubility of solutes may be improved by using reversed micellar emulsion or microemulsion systems in which the solutes are solubilized in the water pools. Highly hydrophobic and CO₂-philic surfactants usually have a fluorocarbon hydrophobic chains[4] which is undesirable due to their high cost and environmental toxicity. The surfactants developed by Mohamed and Eastoe are branched di- or triple hydrocarbonchained ester sulfonates with a high content of methyl groups and a high critical packing parameter. This renders the surfactants soluble even in alkanes.

In our group, a highly hydrophobic surfactant, designed by the Eastoe-group, has been investigated for use as dispersant in *microencapsulation via internal phase separation*[5, 6] which is a very different application as compared to the ones mentioned in the previous paragraph. Yet, control of the interfacial properties is key to successful encapsulation. The internal phase separation method, which was developed by the Vincent group in the late 90ies[5, 7-9], produces hydrophobic uncharged microcapsules consisting typically of a liquid oil core and a semihydrophobic polymer shell[6]. We have explored the possibility to use the branched triple-chained sodium sulfonate; sodium 1,5-dioxo-1,5-bis(3,5,5-trimethylhexyloxy)-3-((3,5,5-trimethylhexyloxy)carbonyl)pentane-2-sulfonate (abbreviated TC4[10], see Scheme 1), in order to form highly charged core-shell particles consisting of a dodecane core and a poly(methyl methacrylate) (PMMA) shell. Charged core-shell particles are beneficial from a colloidal-stability perspective[6, 11, 12] as well as for controlled release of hydrophobic active substances[6, 13]. We have recently investigated the feasibility of using amphiphilic diblock copolymers, carrying a polyelectrolyte block, as dispersants during the microencapsulation. The charges are introduced to the core-shell particle by hydrophobic interaction between the particle and the hydrophobic block.[11, 14] In contrast, this new surfactant-inspired methodology uses TC4 as an oil-soluble

dispersant to anchor, the otherwise non-adsorbing, water-soluble cationic dispersant poly(diallyldimethylammonium chloride) (PDADMAC) on the O/W emulsion droplets by electrostatic interaction[14, 15].

Normally, the use of surfactants as dispersants during microencapsulation using the internal phase separation method prevents the formation of core-shell particles[6]. The reason for this will be discussed in the Section *theoretical considerations*. As an example, Loxley and Vincent studied the effect of using the water-soluble surfactants cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) as dispersants which resulted in partially engulfed oil cores termed *acorn particles*[5]. However, contrary to the current knowledge, we have observed, that the oil-soluble surfactant TC4 enabled core-shell formation. Yet, the observed morphology was multicore-shell rather than single core-shell (see Figure 1)[14]. These findings encouraged us to further investigate the peculiar properties of this highly hydrophobic surfactant. Using surface sensitive techniques, in particular different types of optical tensiometry methods and quartz crystal microbalance with dissipation monitoring (QCM-D), we have investigated the TC4 surfactant at various oil-water, polymer-water and polymer-oil interfaces including its interaction with the polycation PDADMAC which are relevant for the microencapsulation system. The obtained results have been related to the encapsulation and the properties of the PDADMAC-TC4 based microcapsules.

Figure 1. SEM images of microcapsules based on PDADMAC-TC4. (a) is an overview image of the capsules. The capsule in (b) has been subjected to an 3 kV electron beam that gently heated the samples in order to collapse the PMMA shell. The “golf-ball like” indentations reveal the multicore morphology. (c1) and (c2) display cross-sections of 2 weeks old capsules and fresh capsules, respectively, cut with a focused ion beam. Reprinted from reference[14].

2 Theoretical considerations

In this section, the theories concerning microencapsulation *via* internal phase separation will be clarified. In addition, a short introduction to the van Oss formalism and the surface free energy will be provided with a special focus on Lewis acid-base pairs.

2.1 Internal phase separation

The microencapsulation via internal phase separation is strongly dependent on the interfacial tension between the respective phases. The encapsulation starts by the formation of an O/W emulsion[6]. The aqueous phase contains the dispersant (typically a water-soluble polymer such as PVA) and the oil phase contains a volatile solvent

(usually DCM[5, 6, 14] or ethyl acetate[6, 16, 17]), the shell-forming polymer, the core oil (which is a non-solvent for the polymer) and possibly an active substance[6] (see Scheme 1). The internal phase separation and subsequent core-shell particle formation is a result of the continuous evaporation of the volatile solvent which eventually leads to the phase separation of the polymer.

Scheme 1. The microencapsulation process *via* internal phase separation.

Regarding the TC4 based system investigated in this work, the aqueous phase contained the polycation PDADMAC as a water-soluble dispersant and the oil phase contained a small fraction of TC4 as an oil-soluble dispersant (see Scheme 1).

2.1.1 The spreading coefficients

For microencapsulation and *core-shell* formation, it is necessary that the polymer (index p) wets the oil (index o) and aqueous phase (index w), i.e. spreads between the oil and water[6] (see Scheme 1). The spreading coefficient S_p is defined by the free energy for cohesion ΔG_p^c and adsorption ΔG_p^a as;

$$S_p = \Delta G_p^c - \Delta G_p^a = \gamma_{ow} - (\gamma_{pw} + \gamma_{op}) \quad 1$$

The morphology of droplets of three immiscible liquids was derived and explained in terms of spreading coefficients by Torza and Mazon[18]. This theory was later expanded by in particular Loxley and Vincent[5] to also encompass solid polymers[5, 19]. If $S_p > 0$, the polymer will spread between the water and oil. The spreading coefficients for the oil and water phase may be derived in a similar manner. Traditionally, it is assumed that $\gamma_{ow} > \gamma_{op}$ which leads to three possible sets of spreading conditions[5, 18];

$$S_o < 0; \quad S_w < 0; \quad S_p > 0, \quad 2$$

$$S_o < 0; \quad S_w < 0; \quad S_p < 0, \quad 3$$

$$S_o < 0; \quad S_w > 0; \quad S_p < 0, \quad 4$$

The core-shell morphology can only be obtained if the conditions in Equation 2 are satisfied. Equation 3 will generate so called *acorn particles* (usually formed when surfactants are used as dispersants[5, 6]) and Equation 4 will result in separate oil and polymer droplets[6]. It has been suggested that multicore-shell particles may form when $S_p \gg 0$ [20]. If no oil is added during the encapsulation, a homogenous polymer particle or microsphere will form and the spreading conditions have no meaning.

Scheme 2. Possible morphologies and outcomes of the microencapsulation; a) core-shell, b) multicore-shell, c) acorn-shaped morphology and, d) droplet separation.

It is clear that the core-shell formation necessitates that the γ_{ow} remains high. This is the reason why conventional surfactants, which significantly reduces γ_{ow} , cannot be used for microencapsulation purposes. Instead, polymeric stabilizers are the proper choice of dispersants[6].

2.2 The van Oss formalism

The interfacial energy is a result of intermolecular forces and can therefore be separated into additive contributions (ion-ion, ion-dipole, Keesom, Debey, London dispersion)[21] in a similar manner as for the bulk[22].

Scheme 3. Free energy of cohesion of phase i (a) and adhesion of phase i and j (b). In the present case, i represent water and j represents an alkane. Water, being bipolar interacts with both Lifshitz and acid-base components. The interaction energy is therefore denoted ϵ_{ii}^{LW+AB} , following the van Oss formalism. The alkane possesses only London dispersion forces ϵ_{jj}^{LW} and the interaction between water and alkane can therefore only contain London dispersion components. (c) A system containing a strongly adsorbing solute on a solid substrate. The magnitude of the work of adhesion will depend on if the interface is placed between the adsorbed layer and the solid substrate or between the bulk solution and the adsorbed layer.

The most simple representation is the separation of the interfacial energy into a dispersive part γ^d and a polar part γ^p as proposed by Fowkes[23]. However, regarding the polar part, it has been demonstrated that the Debye and Keesom contributions are very small[21, 24]. Moreover, the polar contribution is usually overestimated and neglects the more complicated but important contribution from H-bonding[21, 24]. Following the van Oss-Chaudhury-Good formalism (Equation 5-8), the apolar γ^{LW} contribution is expressed as the total Lifshitz or van der Waals force and the polar term γ^{AB} accounts only for Lewis acid-base interaction. The polar term is expressed by an acid component γ^+ and a base component γ^- (see Equation 6)[21].

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB}$$

5

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-} \quad 6$$

The interfacial tension components may now be expressed by the geometric mean of the usually known surface tension components.

$$\gamma_{ij}^{LW} = \left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}} \right)^2 \quad 7$$

$$\gamma_{ij}^{AB} = 2 \left(\sqrt{\gamma_i^+} - \sqrt{\gamma_j^+} \right) \left(\sqrt{\gamma_i^-} - \sqrt{\gamma_j^-} \right) \quad 8$$

Clearly, γ_{ij}^{LW} will always be positive. However, γ_{ij}^{AB} may attain negative values if i is a strong Lewis base and j is a strong Lewis acid or vice versa[21].

With respect to liquids, a negative interfacial free energy is impossible since the liquid interface cannot store energy (zero shear stress)[21]. In contrast, solid surfaces (nonzero shear stress) may obtain negative interfacial free energies with liquids which is even anticipated for strong Lewis acid-base pairs[21] as described above. This may seem as an anomaly; however, a negative surface energy only implies that the energy of adhesion is larger than the energy of cohesion as exemplified in Scheme 3c. It should be noted that for a strongly adsorbing solute, it may be speculated whether the interface rather should be positioned between the adsorbed layer and the bulk solution (see Scheme 3c). In such a situation, the work of adhesion will be smaller and the interfacial free energy is not necessarily negative. However, in the present study, the interface is defined at the solid surface.

3 Materials and methods

Dichloromethane (DCM), diiodomethane (DIM), glycerol, formamide, acetone, dodecane and PMMA (350 000 g/mol) were all of analytical grade BioReagent or ReagentPlus, >99% (Sigma Aldrich). Milli-Q® ultrapure water system was utilized throughout the work. PDADMAC (350 000 g/mol, 40 wt% in water) was a gift from Eka Chemicals, Bohus, SE and the hydrophobic anionic surfactant sodium 1,5-dioxo-1,5-bis(3,5,5-trimethylhexyloxy)-3-((3,5,5 trimethylhexyloxy)carbonyl)pentane-2-sulfonate (TC4) was kindly provided by Prof. Julian Eastoe, Bristol University. The synthesis of this surfactant has recently been described in the literature[10].

3.1 Microencapsulation

The microcapsules were prepared as previously described by Loxley and Vincent[5] with some small modifications[14], using a Heidolph Silent Crusher M and a high shear homogenizer Heidolph TYP 22 F/M (both from Heidolph Instruments, Schwabach, GE) in a three necked flask. The oil phase (20 g), containing PMMA (0.2 g), dodecane (0.4 mL), TC4 (2.5 mg) and acetone (1 mL) dissolved in dichloromethane (DCM), was slowly added to 20 mL aqueous phase (0.1 wt% PDADMAC dissolved in Milli-Q water) under stirring at 5 000 rpm. The stirring was raised to 7 500 rpm for 1 h. The emulsion was poured into 30 mL aqueous phase and the DCM was allowed to evaporate overnight under vigorous stirring. The microcapsule suspension was subsequently analysed using light microscopy, microelectrophoresis and SEM as described in more detail elsewhere[14].

3.1.1 Purification

The microcapsules were centrifuged at 6 000 rpm on a Beckman Avanti J-20xp centrifuge (Beckman Coulter, Bromma, SE). The particles were collected and resuspended in Milli-Q water.

In addition to centrifugation, ultrafiltration was used. The microcapsule suspension was gently filtrated with a ten-fold volume of Milli-Q water with a nitrogen gas pressure of 4 bars for approximately 3-4 h. The filter was an isopore™ HTTP membrane filter with a pore size of 0.2 µm (Millipore, Solna, SE).

3.2 QCM-D

The adsorption isotherms of the dispersants on PMMA or PMMA functionalized with TC4 model surfaces were measured using a QCM-D E4 instrument (Q-Sense, Göteborg, SE) with a flow rate of 50 µl/min. At least three replicas were performed.

3.2.1 Surface preparation

The crystals were initially cleaned in an UV/ozone chamber for 10 min followed by immersion in a base piranha solution (1:1:6; H₂O₂ (Merck, 25%):NH₃ (Merck, 25%):MilliQ-water) for 10 min at 78 °C. The crystals were rinsed, dried and finally subjected to a second 10 min UV/ozone step.

Nanometer thin PMMA films with or without TC4 were prepared by spin-coating the freshly cleaned crystals with 50 µl of a 1 wt% solution of PMMA in chloroform. Regarding TC4 functionalized surfaces, the solution also contained 0.5 wt% of this surfactant which corresponds to the theoretical concentration of TC4 in the capsule shell normalized by the specific surface area. The crystals were mounted on a home built Teflon support in a Spin 150 spin coater (SPS-Europe, Putten, NE) and spin coated at 2 000 rpm for 60 s. The spin coated crystals were finally heated to 130 °C in a Nabertherm muffle furnace (Nabertherm, Lilienthal, GE) for 1h followed by slow cooling to 90 °C. The thickness of the PMMA film was determined by measuring the frequency shift of the quartz crystal in air before and after spin coating using the Sauerbrey equation[25] (Equation 4), where Δm is the mass change, Δf^n the change in frequency for a given overtone n ($n=1, 3, 5 \dots$), C the mass sensitivity constant ($17.7 \text{ ng} \cdot \text{cm}^{-2} \cdot \text{Hz}^{-1}$), ρ the film density and δ the film thickness.

$$\Delta m = \frac{\Delta f^n C}{n \rho \delta} \quad 9$$

3.2.2 Adsorption isotherms

Regarding the TC4 functionalized PMMA surfaces, the presence of salt in the film affected the piezo-electric resonance and no signal could be obtained if the salt concentration in the medium was below 100 mM NaCl. Therefore, the salt concentration was constant at 100 mM for the TC4 based system and for the PMMA reference system.

The thickness of the *in-situ* adsorbing layer was calculated by applying the Voight model in the software Qtools (Q-Sense, Göteborg, SE).

3.3 Optical tensiometry

The surface tension, interfacial tension and contact angle of the liquids and substrates were determined using a Theta optical tensiometer (Attension, Espoo, FI) by fitting the drop shape with the Young-Laplace equation (Equation 10), where γ is the surface or interfacial tension, $\Delta\rho$ the density difference between the drop and the surrounding medium, g the gravitational constant, R_0 the radius at the drop apex and β the shape factor.

$$\gamma = \Delta\rho g \frac{R_0^2}{\beta} \quad 10$$

For each combination at least three measurements were made. A summary of all combinations of liquids and substrates are presented in the Supporting information. In general, the concentrations of TC4 and PDADMAC in the different phases were adjusted in order to reflect the corresponding concentration in the real microcapsule system unless otherwise stated.

3.3.1 Surface free energy calculations

The surface energy of PMMA and PMMA functionalized with TC4 was calculated using the formalism developed by van Oss and coworkers[24] as described in the theoretical considerations section. The Lifshitz contribution, as well as the polar acid and base contributions, was obtained from measurements of the contact angles of DIM, formamide, glycerol and water on the substrates. The details are presented in the Supporting information.

3.3.2 Dilatational rheology

The surface rheological parameters were obtained by frequency sweeps at constant amplitude using aPD-200 module (Attension, Espoo, FI). In general, an amplitude of 10; which was within the linear regime, was used. The data was processed in the Software Oscdrop 2008 (Attension, Espoo, FI).

4 Results

The structure of TC4 is displayed in Scheme 1. TC4 was practically insoluble in water (CMC=12.5 μ M[10]) but was, as mentioned in the introduction, soluble in non-polar liquids such as DCM and dodecane. The profound solubility in dodecane was rather surprising given that TC4 is a salt. However, this emphasizes the profound hydrophobicity provided by the many methyl groups. TC4 could also be solubilized in pure alcohols such as ethanol and methanol. In addition, mixtures of alcohols and water enabled moderate solubilisation of TC4. For the series of solvents used, the TC4 solubility increased in the order;
water<methanol<ethanol<dodecane<acetone $\approx$ DMC

4.1 Microencapsulation

Only the combination of the TC4-PDADMAC dispersant pair allowed for proper encapsulation. If only PDADMAC was used as dispersant, the microencapsulation resulted in one solid “macrocapsule” (Figure 2a). The use of only TC4 resulted in macroscopic phase separation. A slow macroscopic phase separation was also observed if TC4 was used in high amounts (>0.04 wt% in the oil phase) in combination with PDADMAC at constant a concentration of 0.1 wt% in the aqueous phase. However, for the proper combination of TC4 and

PDADMAC (see Section 3.1), small (mean radius~1.2 μm) and monodisperse (variance~0.19) microcapsules were obtained[14] (see Figure 2b). Moreover, the PDADMAC-TC4 based microcapsules represent to our knowledge the most monodisperse particle system prepared so far using the internal phase separation[5, 14]. The surface charge, as estimated by the ζ -potential (see Supporting information) was high and positive and did not change during the gentle ultrafiltration nor during the more aggressive centrifugation purification process (see section 3.1.1 on page 10) which indicated that PDADMAC adsorbed irreversibly.

Figure 2. (a) Result of microencapsulation using only PDADMAC in the water phase (photo by Ye Li). (b) Light microscope photos of microcapsules prepared with PDADMAC-TC4.

4.2 QCM-D

The adsorption isotherm of PDADMAC on PMMA and PMMA functionalized with TC4 (see Figure 3a) were fitted with the steady state Langmuir adsorption model (see Equation 11) as derived in the appendix. The TC4 content in the PMMA film was 1/3 which may appear to be very high. However, this fraction corresponded to the amount of TC4 in the microcapsule PMMA shell normalized by the specific surface area of the microcapsule PMMA shell and the 10 nm thick spin-coated PMMA film on the QCM-D crystal respectively. This is further motivated in the Supporting information. Γ is the adsorbed amount, Γ_{max} the *maximum adsorbed amount* or *binding site density*, K_{ad} the *equilibrium* or *affinity constant* and c the bulk concentration. The product $\Gamma_{\text{max}}K_{\text{ad}}$ is sometimes called the *binding capacity*.

$$\Gamma = \Gamma_{\max} \frac{K_{\text{ad}} c}{1 + K_{\text{ad}} c}$$

Figure 3. (a) Adsorption isotherms obtained from QCM-D measurements of PDADMAC (a) on a TC4 modified PMMA surface (■, red) and PDADMAC on a pure PMMA surface (■, blue). (b) Adsorption of 0.4 wt% PDADMAC on PMMA as a function of TC4 concentration.

4.2.1 PDADMAC adsorption isotherm

It is interesting to note that although the maximum adsorbed amount $\Gamma_{\max}$ was two orders of magnitude larger for the TC4 functionalized surface as compared with the pure PMMA surface, the affinity constant was essentially equivalent for the two types of surfaces (see Table 1).

Table 1. Parameters from adsorption measurements obtained using QCM-D and pendant drop measurements.

Dispersant combination	QCM-D			Interfacial tension		
	$\Gamma_{\max}$ [ng·cm ⁻²]	K [wt% ⁻¹]	$\Gamma_{\max}K$ [ng·cm ⁻² ·wt% ⁻¹]	γ_e [mN·m ⁻¹]	τ [s]	n

PDADMAC-TC4						
PDADMAC		3 056	3 810	11 643 360	2.57	110.5 1.074
TC4	Hyperbolic	19 970	0.524	10 464		
	Linear			11 590		
TC4	Water				4.01	5.948 1.087
PDADMAC						
PMMA		82.79	3 815			
	Dodecane				51.7	4.526 ^a 2.407 ^a

^aThe fitted dynamic interfacial values should be taken with caution. The noise of the data was very large and the fitted parameters exhibited large standard deviations.

4.2.2 Variation of the TC4 content

The adsorption of PDADMAC at a constant concentration ($c=0.04$ wt%) was measured as a function of TC4 content (see Figure 3b). Note that defining a corresponding TC4 adsorption isotherm has no physical meaning since the TC4 content at the surface is assumed to be constant during the course of the PDADMAC adsorption. However, since K_{ad} appeared to be independent of the presence of TC4, it is more reasonable to assume that Γ_{max} is a function of the TC4 content (see Equation 12). The steady state adsorption is therefore both a function of the TC4 concentration $f(c^-)$ and of the PDADMAC concentration $g(c^+)$ (see Equation 12).

$$\Gamma(c^-, c^+) = f(c^-)g(c^+) = \underbrace{\Gamma_{max}(c^-)}_f \underbrace{\frac{K_{ad}c^+}{1 + K_{ad}c^+}}_g \quad 12$$

The adsorption of PDADMAC as a function of TC4 content was fitted both with a linear and a hyperbolic, Langmuir-like, adsorption model (see Figure 3b and Table 1) by taking into account the adsorption of PDADMAC on the pure PMMA surface containing no TC4, Γ_0 (see Equation 13, 14 and Table 1). Note that the adsorption at $c^+=0.04$ wt% corresponded almost to $\Gamma(c^+ \rightarrow \infty) = \Gamma_{max}$, (see Figure 3a) which means that the symbol of the y-axis in Figure 3b can be replaced with Γ_{max} .

$$\Gamma_{max}(c^-) = \Gamma_0 + \Gamma'_{max} \frac{K'c^-}{1 + K'c^-} \quad 13$$

$$\Gamma_{max}(c^-) = \Gamma_0 + K'c^- \quad 14$$

4.2.3 Adsorption kinetics

The adsorption kinetics of a solute can often be expressed as a decaying exponential function[26] (see Equation 15) where, $\Gamma(t, c)$ is the adsorbed amount as a function of time and concentration, $\Gamma_{\infty}(c)$ is the steady state concentration as $\Gamma(t \rightarrow \infty, c)$ for a given c , τ is the characteristic relaxation time and β is a stretching constant which is 0.5 for diffusion controlled adsorption and 1 for thermodynamic controlled adsorption[26].

$$\Gamma(t, c) = \Gamma_{\infty}(c) \left(1 - e^{-\left(\frac{t}{\tau}\right)^{\beta}} \right) \quad 15$$

However, since the concentration was kept constant during the QCM-D measurements, the non-steady state Langmuir adsorption model is reduced to a linear differential equation which has been derived in the Appendix and which results in Equation 16 where k_{ad} is the rate constant of adsorption.

$$\Gamma(t, c) = \frac{c\Gamma_{\max}}{\xi} \left[1 - e^{-k_{ad}t\xi} \right] \quad 16$$

$$\xi = c + \frac{1}{K_{ad}}$$

Equation 15 and 16 implies that the relaxation time τ should depend on the concentration which was indeed the case (see Supporting information). At very low concentrations, the adsorption process is governed by the rate of desorption k_{de} since $k_{ad}/K_{ad}=k_{de}$. At very high concentrations, $\Gamma_{\infty}(c)$ reduces down to $\Gamma_{\max}$ as predicted by the steady state derivation. Note that Equation 16 has only been used to qualitatively describe the adsorption process. No attempts have been made to extract adsorption constants since the data regarding the adsorption at low concentrations was not of good enough quality and since this regime is usually dependent on diffusion controlled processes[26, 27]. In addition, the adsorption model assumes that the desorption should lead to complete depletion of polymer at the surface which was never the case (see Supporting information) and which is a general feature of polymer adsorption[27]. A fraction of PDADMAC, which scaled with the TC4 content, was always more or less irreversibly adsorbed. However, the rate of adsorption and desorption appeared to be independent of the TC4 content (see Supporting information) which is in line with the steady state results in Section 4.2.1.

4.3 Optical tensiometry

The TC4 surfactant had a very profound surface activity at most water interfaces evaluated including the; air-water[10], dodecane-water and the DCM-water interface (see Figure 4a). However, the interfacial pressure was much more pronounced for the water-dodecane interface as compared with the water-DCM interface. At higher concentrations, the water-dodecane system attained a lower interfacial tension than the water-DCM system (see Figure 4b). The water-dodecane interfacial tension was further reduced to very low values when the water phase contained PDADMAC (see Figure 4a and Figure 5). The effect on the DCM phase was much less pronounced. An interesting notation could be made regarding the PMMA-dodecane interface. If TC4 was dissolved in dodecane, the interfacial pressure for the PMMA-dodecane interface was negative, indicating that TC4 avoided the interface. However, if TC4 was dispersed in the PMMA phase, the interfacial pressure for the PMMA-dodecane interface was positive (see Figure 4a). This indicated that TC4 in PMMA stabilized the PMMA-dodecane interface in contrast to the corresponding situation when TC4 was dissolved in dodecane.

Another interesting observation concerned the PMMA-water interface. We expected that the presence of TC4 at the interface would result in complete wetting of a water droplet. However, this was not observed (see supporting information). It was hypothesized that this was an effect of the spin-coating conditions. It is likely that TC4 would orient its hydrophobic carbon-chains towards the air at the PMMA-air interface during the spin-coating procedure. However, pre-wetting the PMMA-TC4 surface in Milli-Q water with gentle heating had no

effect on the results. Yet, it should be noted that a significant reduction of the interfacial tension was observed (see Figure 4a). In contrast, if PDADMAC was added to the water phase, a very large interfacial tension reduction was observed (see Figure 4a) and the interfacial free energy obtained negative values (see Table 2 and the Theoretical considerations).

Figure 4. (a) Interfacial pressure of TC4 in different phases including; air, dodecane, DCM and PMMA (x-axis), against water (blue bar), water containing PDADMAC (water(+), red bar), PMMA (grey bar) or dodecane (yellow bar). Regarding the interfacial pressure for air-water, the TC4 is residing in the water phase (at extremely low concentrations)[10]. (b) Surface pressure isotherm of TC4 in dodecane (○) and DCM (●). Insert shows the corresponding surface tension isotherm.

4.3.1 Gibbs adsorption isotherms

The interfacial tension decrease for an ionic surfactant is related to the surface concentration Γ according to the well-known Gibbs adsorption isotherm (Equation 17) where R is the gas constant and T is the temperature.

$$\Gamma = -\frac{1}{2RT} \left(\frac{\partial \gamma}{\partial \ln c} \right)_{T,p} \quad 17$$

Mohamed et. al. reported that the TC4 surfactant occupied $53 \text{ \AA}^2/\text{molecule}$ at the air-water interface[10]. From Figure 4b, TC4 was found to occupy $21.5 \text{ \AA}^2/\text{molecule}$ and $71.3 \text{ \AA}^2/\text{molecule}$ at the dodecane-water and the

DCM-water interface respectively. These results appeared to be reasonable; however, the obtained data should be taken with caution and should only be used to compare the two types of interfaces. It was difficult to obtain good enough data since the interfacial tension drops occurred over a very narrow concentration interval. In addition, the inflection point in the isotherm is not a result of micellization since the surfactant is dissolved in the hydrophobic solvent which renders the results more difficult to interpret.

4.3.2 Dynamic surface tension

It is clear from Figure 5 that the relaxation behaviours of the water-dodecane interface for the TC4 and PDADMAC-TC4 system were very different. However, the experimental data could not be fitted with the theoretical adsorption kinetics derived by Sutherland[28] (Equation 7) where $\gamma(t)$ is the dynamic interfacial tension, γ_e the equilibrium interfacial tension, γ_0 the initial interfacial tension, t time and τ the characteristic relaxation time.

$$\frac{\gamma(t) - \gamma_e}{\gamma_0 - \gamma_e} = \exp(t/\tau) \operatorname{erfc}\left(\left(t/\tau\right)^{\frac{1}{2}}\right) \quad 18$$

Therefore, the empirically derived equation for adsorption kinetics proposed by Xi Yuan and Rosen[29], which has the same form as many other relaxation processes (Equation 8), was used to fit the interfacial tension decay of the freshly formed droplet. n is a dimensionless exponent describing the slope of γ . It has been suggested and shown in some cases that more hydrophobic surfactants display a higher value of n [29]. The data are presented in Table 1.

Figure 5. Oil-water interfacial tension decay for the different dispersant systems; w(PDADMAC)-o(TC4) (■, red) and w-o(TC4) (■, blue).

$$\frac{\gamma(t) - \gamma_e}{\gamma_0 - \gamma_e} = \frac{1}{1 + (t/\tau)^n} \quad 19$$

The surfactant TC4 had a small characteristic relaxation time which is logical given its relatively small size. On the other hand, the interfacial tension decay was much slower for the PDADMAC-TC4 system although with a very similar value of n . The slow kinetics is most likely due to the slow continuous adsorption of PDADMAC to the interface. We performed also measurements using only PDADMAC. However, PDADMAC had very little

effect on the water-dodecane interface. The fit contained a large portion of error and the corresponding data are hence omitted.

4.3.3 Surface free energy calculation

The surface free energy components for PMMA and PMMA functionalized with TC4 are presented in Figure 6. The values for pure PMMA were very similar to those obtained from the literature[24] with a small polar character as obtained using the Fowkes approach. Using the van-Oss approach, the polar part (which is not equivalent to the polar part from the Fowkes approach in terms of intermolecular forces) is purely of Lewis base character. When PMMA was functionalized with TC4, the basic character was increased which is reasonable since TC4 is an anionic surfactant. The small acidic contribution was most likely an effect of the presence of Na^+ counter ions. Furthermore, the van Oss results were very similar to the corresponding Fowkes results (see Figure 6). The details of the results are presented in the Supporting information.

Figure 6. Surface free energy parameters for PMMA and PMMA containing TC4 obtained using the van Oss or Fowkes formalism.

4.3.4 Spreading coefficient calculations

Since the TC4 surfactant was readily soluble in dodecane it could not be established whether the surfactant preferred the oil or the polymer phase. That at least a significant portion was located in the PMMA phase was clear due to the detection of a stable and highly positive ζ -potential (see Supporting information) of the colloidal suspension indicating a strong interaction between the microcapsule and PDADMAC in the water phase. Furthermore, TC4 was readily soluble in DCM and since DCM and PMMA have almost equivalent solubility parameters[30], it can be assumed that TC4 is readily dispersible in PMMA. The spreading coefficients (Equation 1) were therefore calculated at the two extremes, *i.e.* by assuming that the surfactant was present in *either* the oil *or* the polymer phase (see Table 2). Regarding the situation where all TC4 was assumed to reside in the oil phase, it was predicted that the oil phase should spread around a PMMA core in the aqueous phase forming an “inverted” core shell particle. On the other hand, when all TC4 was assumed to be present in the PMMA phase, regular core-shell morphology was predicted.

Table 2. Effect of dispersants on the interfacial tensions γ_{ij} and spreading coefficients S_i for the systems investigated. The index p, o and w represent polymer, oil and water, respectively.

Dispersants	γ_{pw}	γ_{po}	γ_{wo}	S_p	S_o	S_w
Oil soluble anionic surfactant and water soluble polycation						
TC4 in dodecane	22.2 ^a	18.4	2.57	<0	>0	<0
TC4 in PMMA	-3.53 ^a	4.48 ^b	51.7	>0	<0	<0

^aObtained from contact angle measurements of a DIM drop on the surface in the aqueous phase. ^bObtained from contact angle measurements of a water drop on the PMMA surface in dodecane on pre-wetted surfaces.

4.3.5 Dilatational rheology

Dilatational interfacial rheology was conducted in order to investigate the properties of the PDADMAC-TC4 layer at the oil-water interface. Measurements were performed both for the DCM-water and the dodecane-water interface. However, it was difficult to obtain proper oscillatory data for the DCM-water interface which could be due to the low viscosity of DCM (0.4 mPas). In general, the elastic and viscous moduli were very low and there was no observed “skin-formation” (see below). On the other hand, the dodecane-water interface could be properly investigated using dilatational rheology (see Figure 7). Moreover, this system is more representative of the microencapsulation system at the later stages of the evaporation (evaporation of DCM renders the droplet more viscous and hydrophobic), where the interfacial tensions and overall interfacial properties are of paramount importance for the encapsulation progress.

Figure 7. Dilational interfacial rheology of PDADMAC adsorption from an aqueous phase on a dodecane droplet containing TC4. Dynamic, storage and loss moduli of a fresh droplet (a1) and an aged droplet (a2) as a function of frequency. (b1) displays the phase angle of a fresh (●) and an aged droplet (○) as a function of frequency. (b2) Visualisation of the PDADMAC skin formation on a dodecane droplet containing TC4 from pendant drop measurements.

It can be seen in Figure 7a1 that the PDADMAC-TC4 layer was dominated by elastic properties. Moreover, these properties did not change with frequency, indicating that the layer behaved as a viscoelastic solid over the investigated frequency interval. Note that the dilatational elasticity depends on changes in the adsorbed amount (*Gibbs elasticity*) as well as the elasticity of the interfacial network[31]. The viscous response arises from dissipation due to friction (surface viscosity)[32] as well as exchange with the bulk. An investigation of the Cole-Cole plot (see Supporting information) revealed that the interface did not behave as a fluid[32]. When the droplet was aged for 10 min, the elastic contribution became even more pronounced (see Figure 7a2). The difference in terms of viscoelasticity between a fresh and an aged droplet is displayed in Figure 7b1 by the phase angle as a function of frequency. The stiffness and brittleness of the aged droplet could be observed visually during the measurements. In Figure 7b2, the liquid of an aged droplet was evacuated by gently reducing the pressure. However, the reduced pressure resulted in a “bag” formation of the droplet rather than a continuous reduction of the area and volume of the droplet. The entire process is displayed in Video 3 (see Supporting information). Clearly, the interface possessed a shape memory provided by the pronounced interfacial elasticity. The stiffness and brittleness of the interface is also clearly visualized in Video 1, Video 2 and Video 3 (see

Supporting information). The oscillation, using a high amplitude, of the aged droplet resulted in ripples in the interfacial skin (see Video 2).

Video 1. (Left). Oscillatory measurements on a fresh droplet. **Video 2.** (Middle). Oscillatory measurements on an aged droplet. The speed of the video has been increased twice. **Video 3.** (Right). Long-term measurements of a freshly formed droplet which enters into the “skin forming” regime. Towards the end, the liquid of the droplet is evacuated by lowering the pressure, displaying the bag-formation in Figure 7b2 and the subsequent skin rupture when a new droplet is formed. The slow, skin-forming part is presented at three times the recorded speed whereas the last bag-forming and skin rupturing part is presented at half the recorded speed.

5 Discussion and conclusions

In the following subsections, the influence of the surface activity of TC4 at the oil-water, water-polymer and oil-polymer interfaces will be evaluated. It will be concluded that the interaction between TC4 in the oil (DCM) or PMMA and PDADMAC in the aqueous phase is key for the core-shell formation as well as for the colloidal stability. In addition, the presence of TC4 at the PMMA-oil interface is most likely the explanation of the multicore-shell morphology.

5.1 TC4 distribution between oil and polymer

The results indicate that at least the majority of the TC4 fraction is residing in the PMMA phase rather than the dodecane phase. The water interfacial pressure for TC4 in dodecane is much higher compared to the corresponding DCM-water system. In addition, the Gibbs adsorption isotherm indicates that the TC4 molecules are more densely packed at the dodecane-water interface compared to the DCM-water interface. The semi-empirical Lundelius rule states that the interfacial affinity increases as the solvency decreases[33] which is a perfectly logical relation. Consequently, TC4 is more soluble in DCM than in dodecane. Since DCM and PMMA have almost equivalent solubility parameters[30] as mentioned earlier, it is reasonable to assume that the solubility/dispersability distribution can be translated from the DCM-dodecane system to the corresponding PMMA-dodecane system.

The same conclusion regarding the TC4 distribution can be drawn by inspecting the interfacial tensions of the microcapsule system (see Table 2) at the two extremes discussed in Section 4.3.4. The total interfacial free energy for the situation when TC4 is present in the oil is larger than for the situation when TC4 is present in the

PMMA phase. Consequently, thermodynamic arguments points towards a predominant TC4 distribution towards the PMMA phase.

5.2 TC4-PDADMAC interactions at the emulsion oil-droplet interface

During the course of the coacervation process depicted in Scheme 1, the emulsion droplet becomes increasingly hydrophobic. This leads to an accumulation of TC4 at the oil-water interface and a subsequent strong adsorption of PDADMAC which increases in magnitude during the evaporation.

The dense elastic PDADMAC layer may also prevent oil migration from the microphase-separated emulsion droplet during the coacervation process. At the later stages of the coacervation, the oil phase and the PMMA phase each contain a portion of DCM (which can be estimated by inspecting the ternary phase diagram in reference[5]). The oil phase will therefore contain a larger fraction of TC4 as compared to the fully DCM-evaporated situation. Consequently, the signs of the spreading coefficients in Equation 1 are hard to predict, in particular S_w (see Supporting information) where $S_w > 0$ clearly favours phase separation of oil and polymer. The slow macroscopic phase-separation observed at higher TC4 concentrations as described in Section 4.1 may suggest such a condition. However, the highly charged PDADMAC-skin on the interface of the emulsion droplet prevents immediate migration of the hydrophobic oil and maintains the integrity of the oil droplet (see Scheme 4). It is clear that the high adsorbed amount of PDADMAC, facilitated by the strong interaction with TC4, at the emulsion droplet is also important for the colloidal stability. As displayed in Figure 2a, the absence of TC4 leads to a very small adsorption of TC4 which cannot prevent coalescence of the oil droplets, which eventually leads to the complete aggregation of the dispersed phase. On the other hand, the strong elastic nature of the thick adsorbed PDADMAC layer prevent coalescence which together with the very low DCM-water and later PMMA-water interfacial tension result in very small and monodisperse microcapsules.

Scheme 4. Proposed distribution of TC4 in the PDADMAC-TC4 based microcapsule.

5.3 TC4-PDADMAC interactions at the polymer-water interface

The QCM-D results reveal that the adsorption is mainly driven by electrostatics. Regarding the pure PMMA surface, such an assumption would lead to an apparent surface charge density of $\sim 1\text{-}10 \text{ e}/100\text{nm}^2$ (corresponding theoretical TC4 or charge concentration of 1.5 mM normalized by the specific surface area of the 10 nm thick

PMMA film on the QCM-D crystal or simply transferred from particles/volume element to particles/area element). This is a 1-2 orders of magnitude larger surface charge density compared to the pure PMMA surface[34] and corresponds rather to a PMMA surface containing a significant fraction of ionisable initiators or comonomers[35]. Since ion adsorption and autoxidation cannot result in such a high surface charge density, it is clear that the adsorption of PDADMAC on a PMMA surface is also determined by hydrophobic interactions. The importance of the hydrophobic interaction is evident by the increased adsorption of PDADMAC on a PMMA or a PMMA-TC4 surface at higher salt concentrations in the bulk[15], which is the predicted behaviour according to theory[27, 36, 37].

Regarding the influence of the charge density on the PDADMAC adsorption, it is more reasonable to assume a linear relationship between the concentration of TC4 and the amount of binding sites (Equation 14) given the discussion in the previous paragraph and the results in Section 4.2.2.

The irreversible nature of the PDADMAC adsorption is evident in the QCM-D measurements and is manifested by the high and stable surface charge density of the microcapsule. Moreover, the strong electrostatic interaction between PDADMAC and TC4 at the PMMA-water interface leads to a negative surface free energy (see Table 2). This seemingly abnormal result is explained in terms of Lewis acid-base interaction in Section 2.2. Note that PMMA functionalized with TC4 has Lewis base properties (see Figure 6) whereas PDADMAC carries Lewis acid sites.

5.4 The polymer-oil interface and the multicore-shell morphology

The behaviour and the distribution of TC4 at the PMMA-oil interface (see Scheme 4) is most likely the reason for the multicore-shell morphology. The conclusions from Section 5.1 indicate that TC4 is predominantly solubilized in the PMMA phase. As a consequence, TC4 will partition to the DCM-PMMA phase rather than the DCM-dodecane phase during the course of the coacervation. Here, TC4 will accumulate at and stabilize the interface between the polymer-rich and the oil-rich phase as depicted in Scheme 4. However, the surfactant-decorated oil droplets will repel each other and prevent coalescence. Note that this electrostatic stabilization in the non-polar environment is of Coulombic character and consequently not the same as the electrostatic stabilization in the aqueous system which is of entropic/osmotic character. This type of electrostatic stabilization has been reported for the surfactant sodium 1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate; more known as AOT, in a non-polar dispersion of PMMA particles[38]. It is therefore likely that the very similar surfactant TC4 behaves in an analogous manner. The stabilized and dispersed oil droplets will ultimately freeze inside the glassy PMMA phase once all DCM has evaporated, thereby, maintaining the original multicore-shell morphology from the initial stages of the coacervation (see Scheme 1). It should be noted that multicore-shell morphology is predicted when $S_p \gg 0$ [20] as mentioned in the *Theoretical consideration*. However, this situation does not apply for the system investigated in this paper since larger S_p 's have been obtained for microcapsules prepared with the block copolymers discussed in the introduction[14]; yet, these microcapsules displayed the regular core-shell morphology.

6 Acknowledgment

The main author is grateful to Kurt Löfgren for building the spin coater mount, to Ye Li for performing measurements on the microcapsules and to Prof. Michael Persson, Prof. Julian Eastoe and Dr. Azmi Mohamed for providing the PDADMAC and the TC4 sample respectively. Prof. Krister Holmberg and Prof. Magnus Nydén are acknowledged for valuable discussions. Christoffer Abrahamsson is acknowledged for helping with and performing the SEM and FIB-SEM measurements. The foundation for Strategic Environmental Research, MISTRA, is acknowledged for financial support

7 Appendix

The Langmuir adsorption at steady state is defined by the rate of adsorption $\partial\Gamma_{\text{ad}}(t,c)/\partial t$ (Equation A. 3) and desorption $\partial\Gamma_{\text{de}}(t,c)/\partial t$ (Equation A. 2) with rate constants k_{ad} and k_{de} respectively. The rate of adsorption is a second order reaction between the concentration of PDADMAC in the bulk c and the amount of free adsorption sites $S(t,c) = \Gamma_{\text{max}} - \Gamma(t,c)$ and the rate of desorption is a first order reaction proportional to the amount of occupied adsorption sites $\Gamma(t,c)$.

$$\frac{\partial\Gamma_{\text{ad}}(t,c)}{\partial t} = k_{\text{ad}}c \underbrace{(\Gamma_{\text{max}} - \Gamma(t,c))}_{S(t,c)=\text{free adsorption sites}} \quad \text{A. 1}$$

$$\frac{\partial\Gamma_{\text{de}}(t,c)}{\partial t} = k_{\text{de}}\Gamma(t,c) \quad \text{A. 2}$$

By defining the equilibrium constant of adsorption, this leads to the well-known Langmuir adsorption isotherm (Equation A. 3).

$$\begin{aligned} \lim(t \rightarrow \infty) &\Rightarrow \frac{\partial\Gamma_{\text{ad}}(c)}{\partial t} = \frac{\partial\Gamma_{\text{de}}(c)}{\partial t} \\ k_{\text{ad}}c(\Gamma_{\text{max}} - \Gamma(c)) &= k_{\text{de}}\Gamma(c) \\ K_{\text{ad}} = \frac{k_{\text{ad}}}{k_{\text{de}}} &\Rightarrow \\ \Gamma(c) &= \Gamma_{\text{max}} \frac{K_{\text{ad}}c}{1 + K_{\text{ad}}c} \end{aligned} \quad \text{A. 3}$$

The adsorption kinetics can often be described by a decaying exponential function[26] as mentioned in Section 4.2.3.

$$\Gamma(t) = \Gamma_{\infty} \left(1 - e^{-\left(\frac{t}{\tau}\right)^{\beta}} \right) \quad \text{A. 4}$$

However, since the bulk concentration is kept constant during adsorption measurements (QCM-D) by a continuous inflow of bulk solution, the non-steady state Langmuir adsorption is reduced to a linear differential equation (Equation A. 5).

$$\begin{aligned} \frac{\partial\Gamma_{\text{ad}}^{\text{TOT}}(t,c)}{\partial t} &= \frac{\partial\Gamma(t,c)}{\partial t} = \frac{\partial\Gamma_{\text{ad}}(t,c)}{\partial t} - \frac{\partial\Gamma_{\text{de}}(t,c)}{\partial t} \Rightarrow \\ &= k_{\text{ad}} \left\{ c\Gamma_{\text{max}} - \Gamma(t,c) \left[c + \frac{1}{K_{\text{ad}}} \right] \right\} \end{aligned} \quad \text{A. 5}$$

Here, the parameter ξ is defined in Equation A. 6.

$$c + \frac{1}{K_{ad}} = \xi \quad \text{A. 6}$$

After the derivation of the differential equation (Equation A. 7),

$$\begin{aligned} \frac{1}{\xi} \ln \left(\frac{c\Gamma_{\max} - \Gamma(t)\xi}{A} \right) &= -k_{ad}t \\ \Gamma(t, c) &= \frac{c\Gamma_{\max}}{\xi} - \frac{A}{\xi} e^{-k_{ad}t\xi} \\ \frac{\partial \Gamma(t, c)}{\partial t} &= k_{ad}A e^{-k_{ad}t\xi} \end{aligned} \quad \text{A. 7}$$

the unknown constant A can be identified by realizing that as $t \rightarrow 0$, the net adsorption/desorption becomes dominated by the rate of adsorption term which results in Equation A. 8. This derivation results consequently also in a kinetic behaviour described by a decaying exponential.

$$\begin{aligned} \frac{\partial \Gamma(t \rightarrow 0)}{\partial t} &= \frac{\partial \Gamma_{ad}(t)}{\partial t} \Rightarrow \\ k_{ad}c(\Gamma_{\max} - \Gamma(t)) &= k_{ad}A e^{-k_{ad}t\xi} \\ \lim(t \rightarrow 0) &= k_{ad}c\Gamma_{\max} = k_{ad}A \Rightarrow \\ A &= c\Gamma_{\max} \Rightarrow \\ \Gamma(t, c) &= \underbrace{\frac{c\Gamma_{\max}}{\xi}}_{\Gamma_{\infty}} [1 - e^{-k_{ad}t\xi}] \end{aligned} \quad \text{A. 8}$$

By adapting a Langmuir adsorption model, it is reasonable to identify Γ_{∞} in Equation A. 9 as the adsorbed amount at steady state (and hence infinite t) in Equation A. 3.

$$\begin{aligned} \Gamma(t, c) &= \Gamma_{\infty}(c) \left[1 - e^{-\left(\frac{t}{\tau}\right)^{\beta}} \right] \\ \Gamma_{\infty}(c) &= \Gamma_{\max} \frac{K_{ad}c}{1 + K_{ad}c} \\ \Gamma(t, c) &= \underbrace{\Gamma_{\max} \frac{K_{ad}c}{1 + K_{ad}c}}_{\Gamma_{\infty}(c)} \left[1 - e^{-\left(\frac{t}{\tau}\right)^{\beta}} \right] \end{aligned} \quad \text{A. 9}$$

The validity of the derived adsorption model in Equation A. 8 is clear by recognizing the identity of $\Gamma_{\max}$ obtained from the steady state and the non-steady state Langmuir adsorption model in Equation A. 10.

$$\begin{aligned} \Gamma(t, c) &= \frac{c\Gamma_{\max}}{\xi} [1 - e^{-k_{ad}t\xi}] \\ \frac{c\Gamma_{\max}}{\xi} &\equiv \Gamma_{\max} \frac{K_{ad}c}{1 + K_{ad}c} = \Gamma_{\infty}(c) \end{aligned} \quad \text{A. 10}$$

These results indicate that τ in Equation A. 4 should be concentration-dependent through ξ .

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