Novel stabilisation of emulsions by soft particles: polyelectrolyte complexes

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ABSTRACT

We put forward the concept of a novel particle stabiliser of oil-water emulsions being the polyelectrolyte complex (PEC) formed between oppositely charged water-soluble polymers, in cases where either polymer alone is incapable of stabilising an emulsion. Using poly(4-styrene sulfonate) sodium salt, PSSNa and poly(diallyldimethylammonium chloride), PDADMAC, of low polydispersity and similar molecular mass, we correlate the behaviour of their mixtures in water with that of emulsions after addition of oil. In aqueous mixtures, spherical particles of diameter between 100 and 150 nm are formed through electrostatic interactions between charged polymer chains. Around equal mole fractions of the two polymers, the zeta potential of particles reverses in sign and emulsions of oil-in-water (o/w) for a range of oils can be prepared which are the most stable to coalescence and creaming. Effects of PEC concentration and oil:water ratio have been examined. All emulsions are o/w and stability is achieved by close-packed particle layers at drop interfaces and particle aggregation in the continuous phase. Increasing the salt concentration initially causes destabilisation of the aqueous particle dispersion due to particle aggregation followed by dissolution of particles at high concentrations; the corresponding emulsions change from being stable to completely unstable and are then re-stabilised due to adsorption of uncharged individual polymer molecules.

INTRODUCTION

An emulsion can be defined as a heterogeneous system of two immiscible liquid phases in which one of the phases (dispersed phase) is dispersed in the other (continuous phase) as drops of microscopic or colloidal size.[1,2] Emulsions are thermodynamically unstable and there is a tendency with time for them to revert to the separated liquid phases. Therefore, in order to protect the formed drops from coalescence, a surface-active material or emulsifier should be added rendering the emulsions kinetically stable.[1]

One way to stabilise emulsions is with surfactant molecules. The mechanism of stabilisation involves the reduction of the interfacial tension between two immiscible phases by adsorption at the oil-water interface.[3] Emulsions can also be stabilised by surface-active polymers. Here, polymer molecules form structured interfacial films that prevent the coalescence of drops.[4] Proteins and polysaccharides are natural polymers of great interest in the food industry.[5] Due to their balanced hydrophilic/lipophilic structure, proteins place themselves at the boundary between an oil and a water phase, thereby contributing to the suppression of the interfacial tension.[6] Their amphiphilic nature, together with the formation of a viscoelastic film at the interface, provides electrostatic and steric stabilisation of emulsions.[7] Many proteins such as caseins,[8-10] whey proteins,[11,12] ovalbumins[13] and bovine serum albumin[14] have been known for decades as emulsifiers. On the other hand, water-soluble polysaccharides are not considered true emulsifiers by colloid scientists as they do not absorb at liquid interfaces.[15-17] Only certain hydrocolloids, such as gum Arabic, are known to exhibit emulsification properties.[15] Their surface activity is related to hydrophobic proteinaceous moieties bonded to the polysaccharide backbone.[16] Garti and Leser also demonstrated however that certain hydrophilic polysaccharides can display emulsification properties even after the removal of protein residues.[16]

A third type of emulsion stabiliser is solid particles. Particle-stabilised emulsions, whose discovery was attributed to Pickering in 1907,[18] have gained special attention due to the enhanced stability to coalescence compared to the common surfactant-stabilised emulsions.[19] Moreover, as certain particles are biologically compatible and environmentally friendly, their use has spread rapidly in the food, biomedicine, pharmaceutical and cosmetic industries. The stabilisation mechanism is based on the strategic location of the solid particles at the interface. This leads to the formation of a rigid barrier that prevents or inhibits coalescence. Such an effect is explained by the partial wettability of the particles at the oil-water interface as described by Finkle *et al*.[20] The stabilisation is linked to the contact angle that the particle makes with the oil-water interface.[21] Emulsion stabilisation by hard or non-deformable particles has been extensively studied and many examples are available in the literature spanning inorganic materials such as silica,[22-24] metal,[25,26] carbon[27,28] and clay[29-31] particles. On the contrary, reports on emulsions stabilised by soft or deformable particles like microgels are relatively recent. Microgels can be defined as cross-linked polymer particles that are swollen by a solvent.[32] The principles of Pickering emulsions cannot be applied entirely to microgel-stabilised emulsions. Due to their softness, microgels behave differently compared with rigid particles as they become deformed at the oil-water interface.[33] This deformability is crucial in understanding the emulsion stability in such systems.[34] Richtering and co-workers have evaluated such behaviour using their own synthesized microgel of poly(*N*-isopropylacrylamide)-*co*-methacrylic acid (PNIPAM-*co*-MAA).[34-37] Destribats *et al*. have worked with a whey protein microgel[38] as well as microgels made of PNIPAM of variable cross-linking degrees.[39-41] Microgel synthesis is however quite involved and some of the monomers are expensive.

The use of mixtures of particles of opposite charge to form aggregates of low overall charge has been shown to be an effective way of preparing surface-active particles *in situ*, capable of stabilising emulsions.[29,42-44] In these cases, the separate particles of negative or positive charge were too hydrophilic to enable emulsion stabilisation. With this in mind, we had the idea of investigating if mixtures of water-soluble polymers of opposite charge could likewise act as stabilisers of oil-water emulsions, wherein systems containing either polymer alone were ineffective. A polyelectrolyte (PEL, also called polyion) can be defined as a polymer consisting of a macromolecule bearing numerous ionisable groups (either cationic or anionic) and low molecular weight counterions to ensure electroneutrality.[45] Due to the charges along the polymer chain, they are hydrophilic and water-soluble. This feature enables them to form complexes with oppositely charged polyelectrolytes, leading to the formation of the so-called polyelectrolyte complex (PEC) or polyion complex (PIC). Their formation is mainly due to electrostatic interactions between the charged domains of two oppositely charged polyelectrolytes.[46-48] Besides this, additional inter-macromolecular interactions such as van der Waals, hydrogen bonding, hydrophobic and dipole interactions are involved in the formation of the complex but are not the driving force for complexation.[46,47] It is well-known that PEC formation can be considered an entropy driven process as it involves the release of counterions initially bound to the ionic groups of the polymer chain leading to an increase of the system entropy.

PECs in solution can show three different kinds of behaviour in terms of solubility depending on the ionic groups and the differences in molar mass of the two polymers.[46,49] Soluble complexes are achieved by mixtures in a non-stoichiometric ratio of polyelectrolytes containing weak ionic groups and a large difference in molar mass. The formation and stability of these aggregates are dependent on the presence and concentration of soluble salts, on the charge ratio of the two polyions and on the pH of the solution. By altering the above conditions, water-soluble PECs can form stable macroscopic homogeneous systems which coexist in solution with insoluble, colloidally stable PECs, or aggregate and precipitate. Secondly, complex formation between polyelectrolytes with strong ionic groups and/or high and similar molecular weight, usually results in highly aggregated, macroscopic heterogeneous systems which tend to flocculate. However, this aggregation process can be stopped at a colloidal level by working at low or moderate ionic strengths, in extremely diluted solutions and in non-stoichiometric charge ratio conditions. Finally, when concentrated solutions of polyelectrolytes of high and similar molecular weight are mixed near stoichiometric ratios, a two-phase system is formed composed of a liquid phase and a PEC aggregate-rich phase. However, at sufficiently low concentrations, soluble complexes can be obtained even when the charges are neutralized.

The aim of this work is therefore to explore if PECs formed in aqueous solution from near-monodisperse anionic and cationic polymers of similar molar mass attain sufficient surface activity to adsorb at the oil-water interface of emulsion drops after addition of oil. To the best of our knowledge, this is the first such use of PECs as soft interfacial particles enabling emulsion stabilisation. We do however acknowledge the literature on protein-polysaccharide mixtures, whose interactions have been studied since 1896 following the pioneering work of Beijerinck.[50] Complex formation is mainly due to electrostatic interactions between oppositely charged domains of each individual biopolymer.[51] The complex at the emulsion droplet surface can enhance emulsion stability compared with emulsions of protein alone by the formation of a thick layer around the droplets that improves the steric stabilisation. The presence of the polysaccharide during the emulsification process leads to a reduction of the droplet size, which causes a decrease in the rate of creaming.[52] Despite the many examples of emulsions stabilised by protein-polysaccharide mixtures in the literature,[53-63] all of them refer to systems in which the protein alone is an emulsifier, unlike in the systems reported here. We first examine the behaviour of aqueous mixtures of an anionic and a cationic polyelectrolyte and characterise the size and charge of the PECs formed. Emulsions are then prepared from the aqueous polymer mixtures and oil and their stability, drop sizes and arrangement of PEC particles around drops is evaluated. The effects of PEL and PEC concentration, salt concentration, oil volume fraction and oil type are investigated. Air-water and oil-water interfacial tensions of planar interfaces are also monitored.

EXPERIMENTAL

Materials

Poly(4-styrene sulfonate) sodium salt, PSSNa, and poly(diallyldimethylammonium chloride), PDADMAC were purchased from Polymer Standard Services (PSS, Mainz) and were used as received. The chemical structures as well as some other properties are shown in Table 1. Two pure samples of PSSNa of different average molecular weight differing by a factor of 6.1 were chosen. The degree of sulfonation of PSSNa is greater than 90% in both cases (from certificate of analysis). The second polyelectrolyte, PDADMAC, has a molecular weight centred at 160 kDa. For the emulsion preparation, six different oils were selected (Table 1). They include non-polar alkanes, aromatic oils and a silicone oil. Prior to use, all the oils were passed twice through a basic alumina column (particle size: 0.06-0.20 mm, Merck kGaA) to remove polar impurities. Water was first passed through a reverse osmosis unit and then a Milli-Q reagent water system (Millipore). After treatment, its surface tension measured with a Krüss K11 tensiometer and Wilhelmy plate was 72.0 mN m^{-1} at 25 °C. Sodium chloride, NaCl (Fisher Chemical, 99.9%), hydrochloric acid, HCl (Fisher Chemical, 37%) and sodium hydroxide, NaOH (Fisher Scientific, >97%) were used as received.

Methods

(a) Preparation and characterisation of PEC aqueous dispersions

Individual polyelectrolyte solutions of different concentrations (0.01-1 g L^{-1}) were prepared by weighing the corresponding amount of each PEL and dissolving them in Milli-Q water. PEL solutions were prepared at their natural pH. The pH of both the individual PEL solutions (1 g L^{-1} PSSNa 6.32; 1 g L^{-1} PDADMAC 5.44) and the PEC solution (prepared from the 1 g L^{-1} individual PEL solutions 5.71) was measured with a pH meter (3510, Jenway). All solutions were kept at room temperature, in the dark and sealed with parafilm to avoid evaporation.

Aqueous PEC dispersions of different mole fraction of PSSNa (x_{PSSNa}) were obtained by mixing known volumes of each individual polyelectrolyte solution of a fixed concentration with a magnetic stirrer (VWR VMS-C7, stirrer speed = 4) at room temperature. All solutions were prepared in 14 mL screw-cap glass vials. Due to the remarkable influence of the mixing procedure on the particle size,[64-67] we decided to work under fixed conditions in order to obtain reproducible results. Therefore, the order of addition was set as follows: water, PSSNa solution, PDADMAC solution. Water and PSSNa solution were added in one shot additions with a micropipette. PDADMAC solution was then added to the above mixture whilst stirring. The addition of PDADMAC was done sequentially every min up to the total desired volume with a micropipette. This was done to allow the added polyelectrolyte to interact with the oppositely charged species present in the vial. For PEC aqueous dispersions with $x_{PSSNa} < 0.3$, each addition was of 2000 µL, for x_{PSSNa} between 0.3 and 0.5 the addition was of 1000 µL, for x_{PSSNa} between 0.5 and 0.8 it was 500 µL and for $x_{PSSNa} > 0.8$ it was 200 µL. With this protocol, the total mixing time for all the samples was around 4 min. After the complete addition of PDADMAC solution, mixing was kept at the same speed for an additional minute.

For the study of the influence of the salt concentration on the stability of complexes, PEC aqueous dispersions were prepared as above. Immediately after preparation, stipulated amounts of solid NaCl were added into each dispersion in order to obtain a NaCl concentration range from 0 to 5 M. To evaluate the effect of pH on the stability of complexes, individual PEL solutions were prepared in 0.01 M NaOH (pH = 12) and in 0.01 M HCl (pH = 2). After that, PEC preparation was performed as described above.

Dynamic light scattering (DLS) was used to determine the size and the size distribution (polydispersity index, PDI) of aqueous PEC dispersions prepared at natural pH with no added electrolyte. Both parameters were derived from the cumulant analysis.[68] Measurements were carried out at 25 °C using a Zetasizer Nanoseries NanoZS (ZEN3600, Malvern Instruments). The instrument was equipped with a 4mW He-Ne laser beam as a light source, operating at $\lambda = 633$ nm under a scattering angle of 173°. To run the measurement, samples were placed in a plastic disposal cuvette of 1 cm path length. The PDI is a dimensionless value defined by the software as $2c/b^2$, where b is the second order cumulant and c is the coefficient of the squared term of the correlation function. The results of both parameters are given as the average of three measurements of 60 s each. The relative standard deviation was lower than 2% and 10% for the size and PDI, respectively. The DLS technique was limited to aqueous PEC dispersions prepared from individual PEL solutions with a concentration < 1 g L^{-1}. The zeta potential was measured at 25 °C by a Zetasizer Nanoseries NanoZS (Malvern Instruments) equipped with a 4mW He-Ne laser beam operating at $\lambda = 633$ nm. Measurements were made by introducing a universal dip cell (ZEN1002, Malvern Instruments) inside a plastic disposal cuvette. The Smoluchowski approximation[69] was used to convert measured electrophoretic mobilities to zeta potentials. Each value was averaged from three parallel measurements of 12 runs each. The refractive indices of water and aqueous PEC dispersions were obtained using a refractometer (M46 313, Hilger) at 25 °C and were 1.333 and 1.380, respectively. Transmittance measurements on aqueous PEC dispersions were carried out with a UV-Vis spectrophotometer (Perkin Elmer Lambda 25) at $\lambda = 400$, 500 and 700 nm. At these wavelengths none of the polyelectrolytes absorb. Samples were placed in a quartz cuvette of 1 cm path length with Milli-Q water being used as a reference. Transmittance (%) values are given as the average of three measurements.

Scanning electron microscopy (SEM) was used to obtain micrographs of the particles. One drop of the aqueous PEC dispersion was applied to a carbon disc and left to evaporate at room temperature for 3 days. Once dried, the disc was coated with a thermally evaporated carbon film (10 nm thick) using an Edwards high vacuum coating unit. Micrographs were taken with a Zeiss EVO 60 scanning electron microscope at a voltage of 20 kV and a probe current of 70 pA. The average particle diameter was calculated from at least fifty individual entities on SEM images with ImageJ 1.47v software. Energy dispersive X-ray spectra (EDX) were also acquired.

(b) Preparation and characterisation of emulsions

The density of the oils was determined using a density meter (DMA 35N, Anton Paar) at 20 °C. Emulsions containing an aqueous PEC dispersion and n-dodecane were prepared in 14 mL screw-cap glass vials. The mixture was emulsified with an Ultra-Turrax homogenizer (IKA® T25 digital) with a dispersing element of 8 mm (stator diameter). Mixing was for 2 min at a constant speed of 13,000 rpm. Immediately after preparation, the emulsion type was inferred from the drop test, by checking the miscibility of a drop of emulsion with both water and oil. Photographs of the obtained emulsions were taken just after preparation and over time to evaluate their stability. Optical micrographs of the freshly prepared emulsions were obtained on a dimple glass slide (Fisher Scientific) with a cover slip (Scientific Laboratory Supplies LTD) using an Olympus BX-51 microscope fitted with a DP50 digital camera. The mean droplet diameter of the emulsion was calculated from at least fifty individual droplets with ImageJ 1.47v. The fraction of water (f_w) released five days after preparation was measured as a height. However, due to the very low volume of oil separated, for the oil fraction (f_o) the oil was removed carefully from above the emulsion with a Pasteur pipette and weighed.

Selected stable emulsions were imaged with cryo-SEM. A small amount of the emulsion was mounted on an aluminium sample holder (diameter ~ 10 mm) with a Pasteur pipette or a spatula depending on its viscosity. The sample was plunged into liquid nitrogen slush at a temperature of -210 °C. The frozen sample was placed inside the cryo preparation chamber (PP3010T, Quorum Technologies Ltd.) and was fractured with a sharp knife at -140 °C under high vacuum. After that, it was coated with platinum to a thickness of ~ 2 nm. The sample was then transferred to a Zeiss EVO 60 SEM chamber for imaging at a voltage of 15 kV and a probe current of 30 pA at -140 °C. In some cases, in order to obtain a clearer image of the sample, sublimation of the surface water (ice) was performed. This step was done at -75 °C for 10 min.

Different sets of emulsions were systematically prepared by varying one of the following parameters: x_{PSSNa}, concentration of the starting PEL solutions and oil volume fraction. Moreover, the effect of salt addition before or after emulsification was also studied. In the first case, the aqueous PEC dispersion contained NaCl before addition of oil, whereas in the second case, 1 mL of a 5 M NaCl solution was added to a pre-formed emulsion. In addition to this, selected emulsions containing different oils were also prepared.

(c) Surface and interfacial tension

The air-water surface tension of aqueous PEC dispersions was measured with a Krüss K11 tensiometer using a Pt Wilhelmy plate at 25 °C. Surface tensions are given as the average of three measurements. After each measurement, the plate was rinsed with ethanol and heated to glowing in a blue Bunsen flame. The interfacial tension between n-dodecane and an aqueous PEC dispersion was measured with the Krüss K11 tensiometer and the du Noüy ring method (Pt-Ir) at 25 °C. The density of the two phases were measured and inputted in the software. The applied correction method was that of Harkins and Jordan.[70] The results of 3 separate measurements were averaged. All measurements were carried out at room temperature unless stated otherwise.

RESULTS AND DISCUSSION

(a) Characterisation of aqueous dispersions of PEC

Before studying the behaviour of emulsions stabilized by polyelectrolyte complexes, a comprehensive study on PEC characterisation at low concentrations was carried out. To gain a deep insight into their formation and properties, aqueous PEC dispersions were first characterised in terms of size and zeta potential along with microscopy. The appearance of aqueous PEC dispersions prepared from 0.1 g L^{-1} individual PEL solutions at different x_{PSSNa} is shown in Figure 1, where x refers to mole fraction using the values of Mw given in Table 1 (148 kDa PSSNa and 160 kDa PDADMAC). When either PDADMAC or PSSNa are in excess (low and high x_{PSSNa}, respectively), solutions are transparent. However, around the point where all the charges are expected to be neutralised, $x_{PSSNa} = 0.56$, the solutions appear slightly opalescent.

Figure 2(a) shows the average diameter of the PEC particles as a function of x_{PSSNa} of the above dispersions. The results for freshly prepared dispersions and for the same 20 days after preparation are included. As seen, particles seem to shrink with time when PDADMAC is in excess. It is worth noting that the values for the individual polyelectrolyte solutions were not measurable with dynamic light scattering. Owing to the long-ranged electrostatic repulsion between charged monomers within the chain, polyelectrolytes adopt a more expanded, rigid rod-like conformation.[71,72] However, when PEC particles are formed, the individual polyelectrolytes do not adopt this conformation anymore as they interact with each other through electrostatic forces. As shown below, particles are spherical of diameter between *ca*. 100 and 200 nm depending on x_{PSSNa}. On the basis of these results, PEC particles obtained when PDADMAC is in excess (low x_{PSSNa}) seem to be slightly larger and, as soon as the mole fraction of the anionic polyelectrolyte increases, the particles become smaller. When PSSNa is in excess ($x_{PSSNa} > 0.5$) the particle diameter remains constant at around 100 nm. These results are in agreement with those obtained by Mende *et al*.[67] with the same polyelectrolyte system (PSSNa-70 kDa and 1000 kDa, PDADMAC-5 kDa and 290 kDa) who found that the particle size does not vary significantly when PSSNa is in excess. The PSSNa-PDADMAC system was also studied by Dautzenberg (PSSNa-66 kDa, PDADMAC-250 kDa).[73] He reported that the sizes of PEC particles seem to increase as long as the proportion of PDADMAC in the mixture increases, again consistent with our results. Nevertheless, in the literature there is not full agreement about the dependence of the particle size on the mixing ratio. Depending on the polyelectrolytes used and their concentrations, different tendencies have been reported. While in some cases[67,74,75] particles with the smallest size are obtained around the point of charge neutralization and the size tends to increase as soon as one of the components is in excess (displaying a minimum), other authors[76,77] show that particles are smaller when one of the components is in excess and the largest size is obtained at the point where all the charges are compensated.

The formation of more compact structures for $x_{PSSNa} > 0.5$ could be related to the experimental procedure. As described earlier, PDADMAC solution was added in different amounts into PSSNa solutions. Therefore, on the left hand side of the plot, the major component was added to the minor while for $x_{PSSNa} > 0.5$, the minor component was added into the major. According to Müller,[64] for the minor-to-major scenario, more equilibrated smaller PEC particles were achieved as the charge sign is never reversed. Applied to our system, for $x_{PSSNa} > 0.5$, a small volume of PDADMAC solution is dosed into a big volume of PSSNa solution. Consequently, the particles are electrostatically stabilised by the excess like-charged component. However, for the major-to-minor case, immediately after exceeding the critical 1:1 stoichiometry the excess oppositely charged component can “cross-link” the secondary particles to form colloidal networks with lower structural density. Similar trends reported by other authors support this hypothesis.[13,65,66] The corresponding plot of the PDI of particles *versus* x_{PSSNa} is given in Figure 2(b). Interestingly, the polydispersity in size is least when the proportion of both polyelectrolytes is about the same. When one of the components is in excess, the PDI increases revealing a minimum. This is consistent with the results obtained earlier.[67,73,77]

Figure 3(a) shows an SEM image of an aqueous PEC dispersion prepared from the 0.1 g L^{-1} individual PEL solutions at $x_{PSSNa} = 0.56$. In general, particles can be considered quasi - spherical despite some aggregation also being detected. The average particle diameter measured from the micrograph of approx. 100 nm is in good agreement with the one acquired by light scattering. The EDX spectra of the particles verified the presence of sulphur (data not shown). The zeta potentials were determined for freshly prepared dispersions and for those 20 days after preparation. As shown in Figure 4, when PDADMAC is in excess ($x_{PSSNa} < 0.54$), the zeta potential is positive since the positively charged polyelectrolyte in excess surrounds the particles. This value decreases slightly as the PDADMAC proportion decreases. On the other hand, when PSSNa is in excess, the zeta potential is negative and increases slightly in magnitude with increasing x_{PSSNa}. These results are in line with the ones obtained by other authors.[75,77,78] There is a dramatic change in both the sign and value of the zeta potential at x_{PSSNa} between 0.54 and 0.56. This region refers to complete charge neutralisation and fits with the PDI plot, where the particles are least polydisperse.

The same experimental procedure was applied for aqueous PEC dispersions prepared from the 0.5 g L^{-1} individual PEL solutions at different x_{PSSNa} to corroborate the above tendencies. As depicted in Figure 5(a), dispersions become noticeably more turbid as soon as x_{PSSNa} approaches 0.56. The transmittance of these dispersions is given in Figure 5(b). The increase in turbidity around the charge neutralisation point may be attributed to an increase in the overall particle concentration. The possibility of particle aggregation was discounted from the light scattering measurements as the smallest particles were obtained when both charges were neutralised (Figure S1(a)). For this set of PEC dispersions prepared at a higher concentration, profiles for the average particle diameter, PDI in particle size and zeta potential (Figure S1 and Figure S2) were entirely consistent with the ones obtained at the low concentration range. The SEM image of the PEC dispersion (x_{PSSNa} = 0.56) from the 0.5 g L^{-1} individual PEL solutions is shown in Figure 3(b). Here, the concentration of particles is seen to be higher than in the previous case. It is likely however that the film of aggregated particles observed is most likely formed during the slow evaporation process during sample preparation. Finally, to evaluate the influence of the PEL concentration on the structural parameters of the obtained particles, solutions of higher concentrations were prepared at a constant $x_{PSSNa} \approx 0.54$. As shown in Figure 6(a), the higher the initial PEL concentration, the more turbid the dispersion (Figure S3(a)). From the dynamic light scattering measurements, Figure 6(b), it can be concluded that particles seem to aggregate as both the average diameter and the PDI increase with the polyelectrolyte concentration. This can be gleaned from the results of Starchenko *et al.*[79] for the same polyelectrolyte system. By increasing the PEL concentration, and consequently the concentration of primary particles, it accelerates the aggregation and increases the size of the secondary particles.[79,80] The zeta potential of the particles appears to increase slightly with particle concentration until it reaches a plateau around -38 mV (Figure S3(b)).

In order to judge the influence of the polymer molecular weight on the structural parameters of the formed PECs, a set of aqueous PEC dispersions at different values of x_{PSSNa}

were prepared from PELs of different molecular weights: PDADMAC (160 kDa) and PSSNa (976 kDa). As shown in Figure S4, no remarkable differences in either the size or PDI are observed in comparison to the previous results where both polymers were of comparable Mw, although the value of x_{PSSNa} at neutralisation is considerably lower as expected. The average diameter for the PEC particles with $x_{PSSNa} > 0.25$ (anionic polyelectrolyte in excess) is approx. 25 nm larger than that for particles prepared from PEL of similar Mw. Generally, small complexes are formed by small polyelectrolytes, while larger polyelectrolytes give larger complexes.[65,66,81] Ankerfors *et al.*[82] related this tendency to the diffusion-controlled formation of "pre-complexes". While low Mw polymers form stable complexes quickly, larger polyelectrolytes are more prone to aggregation due to longer diffusion times. However, the results presented in this study do not follow the above general tendency, also reported in refs. 80 and 83 for the same pair of polyelectrolytes. Dautzenberg[83] attributed this surprising result to the kinetics of the process of PEC formation that prevails and supresses the effect of the molecular weight on the resulting structures. For the zeta potential data given in Figure S5, slightly higher negative values were achieved for $x_{PSSNa} > 0.25$ compared to the results from polymer mixtures of the same Mw. This can be attributed to the increase in the amount of negatively charged groups on each PSSNa chain.

(b) Oil-water emulsions prepared from polymer mixtures

(i) Systems without salt

Our interest here is whether the PEC particles prepared in water are surface-active enough to adsorb to an oil-water interface created on emulsifying the aqueous phase with a non-polar alkane. We evaluate the effect of three parameters on the emulsion behaviour. Two of them are related to characteristics of the aqueous PEC dispersion (x_{PSSNa} and PEL concentration) whilst the other is the oil volume fraction (ϕ_o). Emulsions of n-dodecane (ϕ_o = 0.2) and an aqueous PEC dispersion from the 20 g L^{-1} individual PEL solutions were prepared for different values of x_{PSSNa} from 0 to 1. From Figure 7(a), it can be seen that oil-in-water (o/w) emulsions prepared with the polyelectrolytes alone (x_{PSSNa} = 0 and 1) are extremely unstable and phase separate completely immediately after preparation; *i.e.* the polymers are not surface-active. This finding contrasts that in the field of emulsions stabilized by protein-polysaccharide complexes, for example, where one or both components stabilize the emulsion alone.[53-63] However, once PECs are present in the aqueous phase, long-term stable o/w emulsions are achieved, implying that PEC particles are the stabilizing emulsifier. These emulsions cream with time with water separating below the cream, apart from the emulsion prepared close to charge neutralization (x_{PSSNa} = 0.52) which is stable. The fractions of water (due to creaming) and oil (due to coalescence) released one week after preparation are plotted in Figure 7(b). In both cases, a minimum is achieved for x_{PSSNa} around 0.5, and the extent of coalescence is extremely small (< 0.05) for all the polymer mixtures. The average droplet size of the emulsions immediately after preparation is given in Figure 7(c) and passes through a shallow minimum value of *ca*. 15 μm for x_{PSSNa} around 0.5, consistent with the inhibition of creaming at this condition. Optical micrographs of some of the emulsions are shown in Figure 8 where all droplets are spherical. It thus appears that, by reducing the overall charge of PEC particles in mixtures of polymers, their hydrophobicity is increased to such an extent that they prefer to adsorb to the oil-water interface during mixing. This argument was used to explain the stabilization of emulsions at optimum ratios of anionic and cationic solid particles.[42,44]

Depending on the initial emulsifier concentration, two main régimes are distinguished with respect to emulsion formation in particle-stabilised emulsions.[84] When the system is emulsified at low concentration of stabilizer, known as the emulsifier-poor régime, droplets are partially covered with the emulsifier. Therefore, once the agitation is stopped, droplets coalesce to a limited extent. The degree of interface coverage by particles increases leading to a reduction of the total interfacial area between oil and water. This prevents further coalescence events.[85] In this régime, the mean drop size decreases with increasing emulsifier concentration. In contrast, at high emulsifier concentrations (emulsifier-rich régime) the average drop size is practically independent of the stabilizer concentration and is mainly governed by the process of drop fragmentation. For emulsions experiencing limited coalescence, the following equation can be written, considering complete adsorption of spherical particles at the interface,[86]

$$\frac{1}{D_{[3,2]}} = \frac{1-\phi_o}{6\phi_o \tau} c \qquad (1)$$

where ϕ_o is the volume fraction of the dispersed phase, c is the initial emulsifier concentration, τ is the stabilizer adsorption density and $D_{[3,2]}$ is the Sauter mean diameter obtained from

$$D_{[3,2]} = \frac{\sum_i N_i D_i^3}{\sum_i N_i D_i^2} \quad (2)$$

where N_i is the total number of droplets with diameter D_i.

By plotting the inverse of the mean drop diameter *versus* the concentration of the emulsifier, a straight line is expected to be obtained. From the slope, the stabilizer adsorption density can be calculated. For that purpose, a series of emulsions of n-dodecane-in-water (ϕ_o = 0.2) were prepared from an aqueous PEC dispersions at $x_{PSSNa} \approx 0.5$ from the individual PEL solutions at different concentrations. The appearance of selected emulsions can be seen in Figure 9(a). At low concentrations (< 0.1 g L^{-1}) no stable emulsions were achieved. However, as soon as the starting PEL concentration increased, emulsions stable to coalescence were formed. For the emulsions prepared with a [PEL] ≥ 20 g L^{-1} the emulsions also showed no sign of creaming and their viscosity increased considerably. The droplet sizes of the stable emulsions were determined directly from optical micrographs and are plotted as a function of the polyelectrolyte concentration in the aqueous phase in Figure 9(b). In the inset, the plot corresponding to eq. 1 is also given. The linear relationship confirms that these emulsions experience limited coalescence in the emulsifier-poor régime. For the explored concentration range, the transition towards the emulsifier-rich régime was not reached and droplets with average diameter as low as 8 μm are formed. From the slope of the graph, the calculated adsorption density by particles is 0.13 g m^{-2}. Without knowing the particle density, it is difficult to compare this value with that expected for close packing of monodisperse particles. An alternative form of eq. 1 given in ref. 85 is based on the number of particles used to estimate the surface coverage. However, this cannot be calculated at present and attempts to determine it by evaporating an aqueous PEC dispersion and imaging it with SEM proved difficult as NaCl crystals masked some of the particles.

Cryo-SEM analysis was attempted with several o/w emulsions around the composition $x_{PSSNa} \approx 0.5$. At a relatively low initial PEL concentration, Figure 10(a) shows part of a dodecane drop partly covered by discrete PEC particles. The frozen oil constituting the drop has been removed allowing visualization of the interface. The particle diameter estimated from the image (230 nm) is comparable to that measured for particles in water with dynamic light scattering (250 nm). In Figure 10(b) and 10(c), emulsion droplets obtained from the PEC solution prepared from 25 g L^{-1} PEL solutions are shown at two magnifications. In this case, the frozen water has been sublimed to better visualize the particles. PEC particles are seen to be densely packed at the oil-water interface and excess particles form a network in the continuous aqueous phase. This dual location of particles explains the excellent stability of emulsions to both coalescence and creaming. A preliminary experiment aimed at establishing the percentage of particles adsorbed yielded the following: starting with 9.6 g L^{-1} PEC in water, the resolved aqueous phase after creaming of the o/w emulsion contained 5.4 g L^{-1}, *i.e.* 56% was non-adsorbed at this relatively high concentration. Closer inspection of Figure 10(c) and Figure S6 may indicate that more than one particle layer exists at the droplet interface; however it may be that these thicker layers are those responsible for the bridging between neighboring droplets.

In order to establish whether catastrophic phase inversion is achievable in this system, the influence of the oil volume fraction was studied by fixing both the polyelectrolyte concentration in the final emulsion (8 g L^{-1}) and the value of x_{PSSNa} (0.54). The appearance of the emulsions at ϕ_o between 0.1 and 0.8 is shown in Figure 11. Upon increasing ϕ_o, all emulsions are o/w in which the volume of emulsion prepared also increases until all the oil and water mixture becomes emulsified at $\phi_o \geq 0.5$. Emulsions at higher oil fractions were noticeably more viscous but completely stable for at least 6 months. The average droplet diameter determined from optical micrographs decreased from 133 ± 32 μm at $\phi_o = 0.1$ to 10 ± 4 μm at $\phi_o = 0.6$. For this polymer mixture and oil chosen, catastrophic inversion cannot be achieved. The preferred emulsion at $\phi_o = 0.5$ being o/w implies that the PEC particles so formed are only partially hydrophobic.

(ii) Effect of salt concentration

One important parameter that influences PEC formation and final structure is the concentration of salt as its ions interact with the charges on the oppositely charged polyelectrolytes. For this reason, its influence on both aqueous PEC dispersions and emulsion stability was evaluated. Salt was added after PEC formation. The appearance of aqueous PEC dispersions prepared at different NaCl concentrations (from 0 to 5 M) from the 1 g L^{-1} PELs solutions at $x_{PSSNa} = 0.52$ is shown in Figure 12(a). Three different regions can be distinguished. Between 0 and 0.1 M NaCl, turbid stable dispersions are obtained. The transmittance at 700 nm decreased from 39% (no added salt) to 13% (in 0.1 M NaCl). The average diameter of the PEC particles was 294 nm without salt and 873 nm in the presence of 0.1 M NaCl, with a broad size distribution in both cases (PDI > 0.3). Moreover, after allowing the dispersions to stand for a couple of days, precipitation of white PEC aggregates was visible at the bottom of the vessel. Taken together, the evidence suggests that the colloidally stable particles without salt begin to aggregate due to the screening effect of the counterions (Na^+ and Cl^-). The second region, between 0.15 M and 3.0 M NaCl, is where flocs of PEC aggregates of several hundred microns appear. Within this range, the floc concentration decreases with salt concentration. Finally, for aqueous PEC dispersions prepared at [NaCl] ≥ 3.5 M, they were completely transparent. However, immediately after salt addition, white flocs were obtained which rapidly dissolved with time. The absence of colloidal particles in these solutions was confirmed through dynamic light scattering. At such high ionic strength conditions, electrostatic interaction between the PELs no longer exists because of the high screening effect of the counterions. Therefore, the PEC particles dissolve liberating the initial soluble chains of both polyelectrolytes which remain unchanged for over 3 months. Our findings are in good agreement with those of a very recent study by Zhang *et al*.[87] for the same pair of polyelectrolytes but of higher polydispersity. Without added salt, neutral small size primary particles surrounded by excess polyelectrolyte were formed (stable PEC). At intermediate salt concentration, small counterions screened the PECs leading to aggregation in large secondary particles that eventually precipitated (unstable PEC). At even higher salt concentrations, dissolution of PECs into the individual chains occurred.

From these dispersions/solutions, emulsions containing n-dodecane (ϕ_o = 0.2) were prepared by the standard procedure. Their appearance immediately after homogenisation is shown in Figure 12(b). Three different scenarios can be differentiated which correlate with the three regions described above for aqueous PEC dispersions. Emulsions prepared with a salt content between 0 M and 0.1 M were o/w and stable to coalescence. Those prepared at [NaCl] between 0.15 M and 3.0 M exhibited complete phase separation as if no polymer mixture was present. Emulsions prepared at salt concentrations greater than 3.5 M were o/w and stable again. We thus see that emulsions stabilised by PEC particles are stimuli-responsive being destabilised and subsequently re-stabilised by salt addition and their behaviour is closely linked to the properties of the pre-cursor aqueous dispersion/solution. The average droplet diameter was measured from optical micrographs for the stable emulsions. By increasing the salt concentration from 0 M to 0.1 M, the droplet size increased progressively and at very high ionic strengths the droplet size was relatively small as shown in the optical micrographs of Figure 13(a). We plot the average droplet diameter as a function of NaCl concentration in Figure 13(b). The increase of the droplet diameter in the first region is related to the aggregation process of particles in water before emulsification. Moreover, the overall PEC concentration decreases due to this aggregation process. In the second region, aggregation levels are exceptionally high. The inability to stabilise any emulsion may be due to a change in the hydrophobicity of the particles following salt addition at this level or to the fact that very large aggregates are easily dislodged from droplet interfaces if they initially adsorb. In the third region, we unexpectedly find that stable emulsions appear again, this time stabilised by individual polyelectrolyte molecules. The average droplet diameter for these emulsions (17 µm) was even lower than the one achieved for the initial emulsion with no added salt stabilised by PEC particles (103 µm). Moreover, during emulsification, a volume of foam was created which was not observed for any of the other emulsions. This suggests that the polyelectrolyte molecules have become surface-active in this high concentration of salt. As a result, we decided to investigate briefly the behaviour of the polyelectrolytes alone dissolved in 5 M NaCl. In Figure S7(a), the appearance of 1 g L^{-1} individual PEL solutions in 5 M NaCl after hand-shaking for 30 s is shown for both polymers. A compact foam was only obtained for PSSNa, implying this polyelectrolyte becomes surface active at the air-water interface. Similarly, the emulsification of both polyelectrolyte solutions with dodecane (ϕ_o = 0.2) was attempted (Figure S7(b)). During homogenisation, air bubbles were formed in both cases but were smaller and more compact in the case of PSSNa. For both polymers, a stable o/w emulsion below the foam was formed, confirming their surface activity when alone at the oil-water interface. There is literature reporting that polyelectrolytes at high ionic strength behave as neutral polymers due to the neutralisation of the ionized groups,[88,89] but we are unaware of studies demonstrating the stabilisation of emulsions in this case.

The influence of salt on an already prepared o/w emulsion was also evaluated by adding 1 mL of 5 M NaCl solution to 5 mL of emulsion resulting in an overall salt concentration in the emulsion of 1 M. This final concentration was chosen as complete phase separation was obtained when salt was added before emulsification. Surprisingly, in this case no phase separation was achieved and the o/w emulsion was stable, although with a larger droplet size (163 µm) compared with the emulsion prepared with no added electrolyte (103 µm). The effect of salt is thus not as pronounced if added after emulsification. Here, salt is not only added after PEC formation (compared to earlier) but also after their adsorption to the oil-water interface. It is conceivable that salt ions dissolved outside of droplets may not access all parts of interfacially bound particles but the origin of the difference needs to be probed in a future study.

The influence of pH on both aqueous PEC dispersions and emulsions was also evaluated (not shown). Both PSSNa and PDADMAC are strong polyelectrolytes dissociating completely in the entire pH range. The influence of pH would be negligible for each polyelectrolyte alone. However, its influence is very relevant upon complex formation as the ion concentration increases due to addition of HCl or NaOH used to prepare the acid and basic solutions. The behaviour was evaluated at pH 2 and 12 for aqueous PEC dispersions prepared from 1 g L^{-1} individual PEL solutions. Their appearance was similar to those obtained from the polyelectrolyte mixture at natural pH (Figure 6(a)). The transmittance decreased from 39.0% for the PEC prepared at natural pH to 26.4% and 32.9% for the PEC dispersions prepared at pH 2 and 12, respectively. Therefore, the same effect as the one obtained after salt addition was noticed. Emulsions prepared from these dispersions and dodecane (ϕ_o = 0.2) either completely phase separated (pH = 2) or contained much larger droplets (660 μm, pH = 12) compared with that prepared at natural pH (103 μm). More work is required to understand the origin of these effects.

(iii) Variation of oil type

The study until now has been with a non-polar alkane which has no groups to modify the surface properties of PEC particles. In order to establish how generic this novel emulsion stabilisation mechanism is, we prepared emulsions from aqueous PEC dispersions from 50 g L^{-1} individual PEL solutions and different oils. Their appearance and optical microscope images are given in Figure 14 for a long chain alkane, an ester, an aromatic oil, a silicone oil and a commercial paraffin. In all cases, o/w emulsions stable to coalescence were obtained. The average drop diameter was approx. 20 μm for all oils except toluene for which it was ≈ 60 μm. We also verified that emulsions with the different oils containing each polyelectrolyte alone (25 g L^{-1}) exhibited complete phase separation after mixing, confirming that the PELs are not surface-active alone.

(c) Behaviour at air-water and oil-water planar interfaces

Finally, in the light of emulsion stabilisation by PEC particles above, we have investigated their surface activity at planar air-water and oil-water interfaces *via* interfacial tension measurements. Aqueous PEC dispersions varying in x_{PSSNa} from 0 to 1 obtained from 0.5 g L^{-1} PEL solutions were prepared. As shown in Figure 15(a), the air-water surface tension of all the dispersions and solutions, including the ones in which the polyelectrolytes alone are present, is 72.0 ± 0.4 mN m^{-1} representing no reduction compared to that for pure water. The surface tension for an aqueous PEC dispersion at higher concentration (1 g L^{-1}, x_{PSSNa} = 0.53) was also 72.0 mN m^{-1}. The PELs and PECs do not therefore lower the tension of the air-water surface, as shown earlier for sodium polyacrylate.[90] Likewise, the dodecane-water interfacial tension was measured for aqueous PEC dispersions prepared from 1 g L^{-1} PEL solutions at different x_{PSSNa}, Figure 15(b). In the absence of polymer, the interfacial tension of 52.6 ± 0.2 mN m^{-1} is in agreement with the value reported in ref. 91 of 52.5 mN m^{-1} confirming the absence of surface-active impurities. Here however, all polymer-containing dispersions/solutions exhibit a lower tension than the bare interface and the tension passes through a shallow minimum at intermediate values of x_{PSSNa}. The maximum lowering however is only *ca*. 10 mN m^{-1} compared with low molar mass surfactant systems which typically lower interfacial tensions to *ca*. 1-5 mN m^{-1} above their critical micelle concentration.[92] As with emulsions stabilised by hard particles, the reduction of the interfacial tension is not the operative mechanism. We are not in a position however to say what level of tension reduction is required for the classical picture of emulsion formation as observed with surfactants. Further, these may not be equilibrium tensions as an energy barrier to adsorption of PEC particles may not be surmounted in the absence of stirring. The findings are in line with those of several authors interested in adsorption of particles from bulk water. Drelich *et al*.[93] found that the paraffin oil-water tension in the presence of hydrophobic fumed silica particles was not significantly different from the value obtained without particles. Similar results were obtained by Vignati *et al*.[94] with silanized silica particles at isooctane or octanol-water interfaces. Even though particles strongly adhered to the interface of emulsion drops, no reduction of the interfacial tension was detected. Aveyard *et al*.[95] found that polystyrene latex particles spontaneously adhere to the octane-water interface, lowering its tension by approximately 4 mN m^{-1}. Importantly, only when *spread* monolayers of particles are compressed and particles in close proximity exhibit mutual repulsion, does the interfacial tension reach very low values (< 2 mN m^{-1}). Thus, the modest lowering mentioned above for *adsorbed* films does not imply that PEC particles are surface-inactive at the oil-water interface.

CONCLUSIONS

We demonstrate the use of polyelectrolyte complexes as novel oil-water emulsion stabilisers using relatively monodisperse polyelectrolytes of PSSNa and PDADMAC of similar molecular mass. We confirm that the anionic and cationic polyelectrolytes alone are not emulsifiers as complete phase separation occurred immediately after mixing. The polyelectrolyte complex formed in mixtures through electrostatic interactions yields particles of between 100 and 150 nm in diameter depending on the ratio of polymers. Oil-in-water emulsions for a range of oils at different oil:water ratios can be prepared exhibiting exceptional resistance to coalescence. The most stable emulsion to both creaming and coalescence is formed at around equal mole fraction of the two polymers, and it possesses the smallest drop size. The average drop size could be tuned depending on the initial polyelectrolyte concentrations. Using cryo-SEM, we observe that particles are located at the oil-water interface of emulsion drops. Their distribution is not uniform at low polyelectrolyte concentrations, whereas at high concentrations a close-packed layer of particles covers the interfaces and excess particles aggregate in water enhancing emulsion stability. The addition of increasing concentrations of salt to aqueous particle dispersions causes a transition from stable dispersions to aggregated and unstable dispersions and finally to dissolution of the particles of complex yielding solutions of the individual polymer molecules. The corresponding emulsions are initially destabilized completely at intermediate salt concentrations but, at high salt concentrations, emulsions are re-stabilised in this case by adsorbed polymer molecules.

We suggest a number of strategies as future directions in this emerging area of soft matter science: (i) *Influence of type of electrolyte*-it has been shown that PEC formation in water is influenced by the radius and valence of the ions in added salt,[96] but nothing is known in emulsions stabilized by such complexes; (ii) *Variation of polymer charge density*-what changes occur in mixing a strong and a weak polyelectrolyte instead of two strong polyelectrolytes as reported here? Detailed studies on this are now underway in our laboratory; (iii) *Investigate the morphology of adsorbed PEC particles*-using novel electron microscope techniques, can we ascertain whether PEC particles adsorb to droplet interfaces as spherical entities or deform once adsorbed akin to certain microgel particles?[41]; (iv) *Increase the hydrophobicity of PEC particles*-by careful selection of the precursor polymers, can we design PEC particles of relatively high hydrophobicity and hence explore their potential as stabilizers of water-in-oil emulsions?; (v) *Simulations*-PEC formation in water has been widely studied using Monte Carlo simulations,[96-99] including the effects of adding salt.[100] Can these simulations be extended to the behaviour of PEC particles at fluid interfaces?

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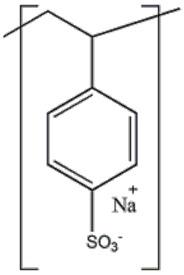
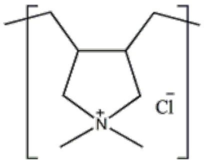
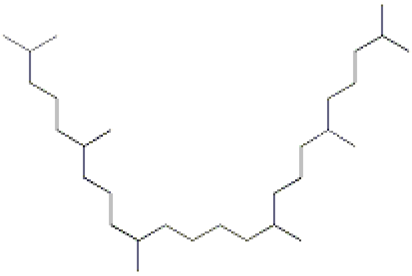
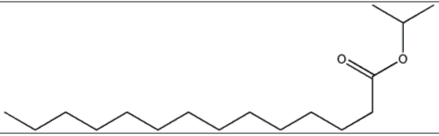
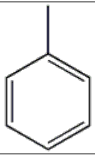
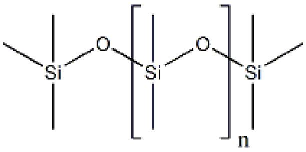
Table 1. Molecular characteristics of polyelectrolytes employed in PEC formation and chemical structure, source, purity and density (20 °C) of all the oils used.

Polyelectrolyte	Repeat unit	Molar mass per charged unit/g mol^{-1}	Mw[a]/Da	Mn[b]/Da	Mp[c]/Da	PDI[d] (Mw/Mn)
PSSNa		207.20	148,000	-	152,000	< 1.20
		207.20	976,000	-	976,000	< 1.20
PDADMAC		161.67	160,000	101,000	-	1.58

Name	**Structure**	**Supplier**	**Purity/ %**	**Density/ g cm^{-3}**
n-dodecane		AlfaAesar	>99	0.796
Squalane		Aldrich	≥99	0.818
***Iso*propyl myristate**		Aldrich	>98	0.859
Toluene		Analar Normapur	100	0.866
50 cS polydimethyl siloxane (PDMS)		Dow Corning	100	0.964
Paraffin oil	Mixture of hydrocarbons from petroleum	Sigma-Aldrich	-	0.869

[a]Mw: Weight average molecular weight; [b]Mn: Number average molecular weight; [c]Mp: Molar mass at the peak maximum; [d]PDI: Polydispersity index

Figure 1. Appearance of freshly prepared aqueous PEC dispersions prepared from the 0.1 g L^{-1} individual PEL solutions at different x_{PSSNa} (given). Scale bar = 1 cm.

Figure 2. (a) Average particle diameter and (b) PDI in size for aqueous PEC dispersions prepared from 0.1 g L^{-1} individual PEL solutions *versus* x_{PSSNa} for freshly prepared dispersions (unfilled circles) and 20 days after preparation (filled circles).

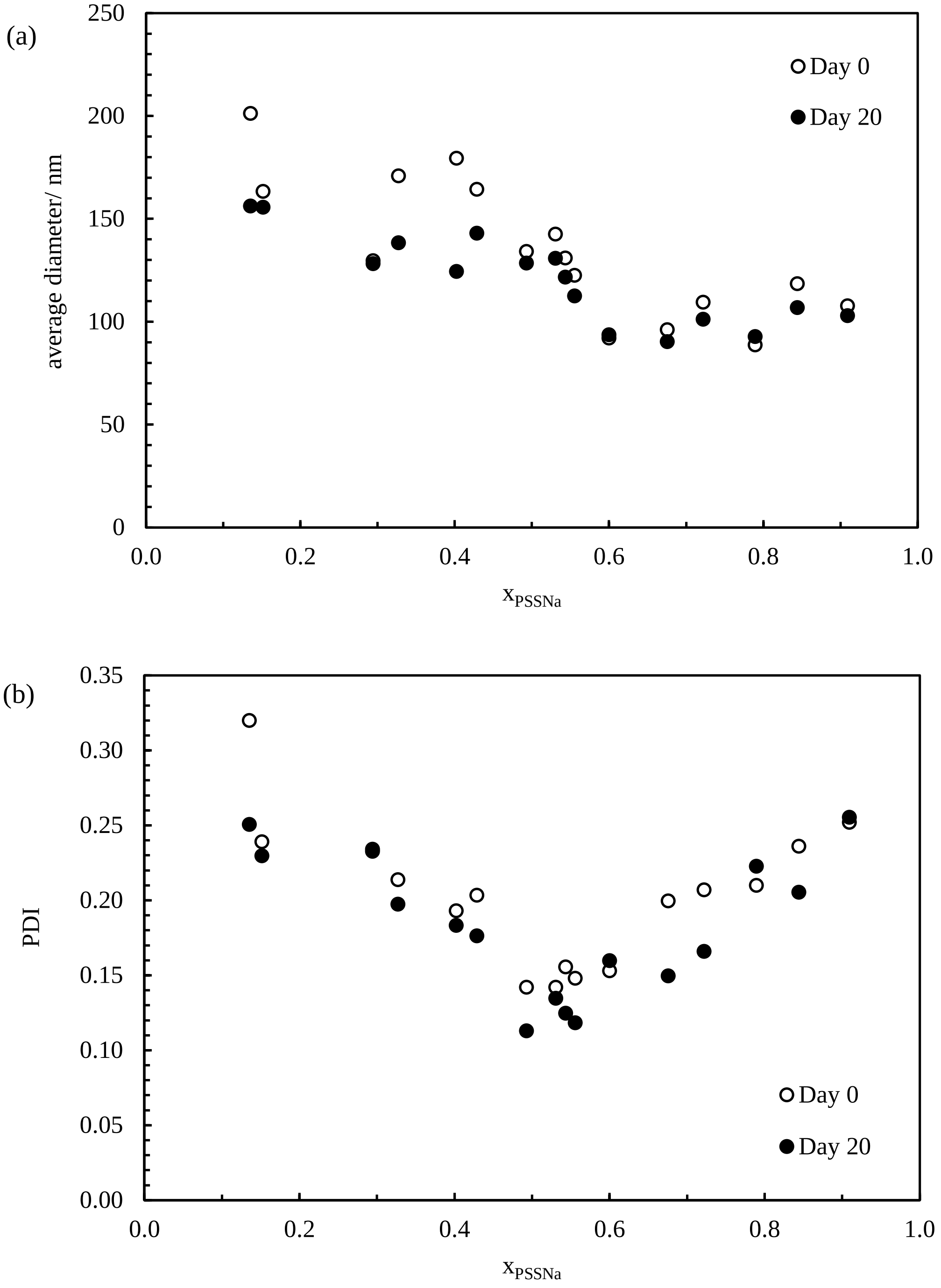


Figure 3. SEM images of aqueous PEC dispersion (x_{PSSNa} = 0.56) prepared from (a) 0.1 g L^{-1} and (b) 0.5 g L^{-1} individual PEL solutions.

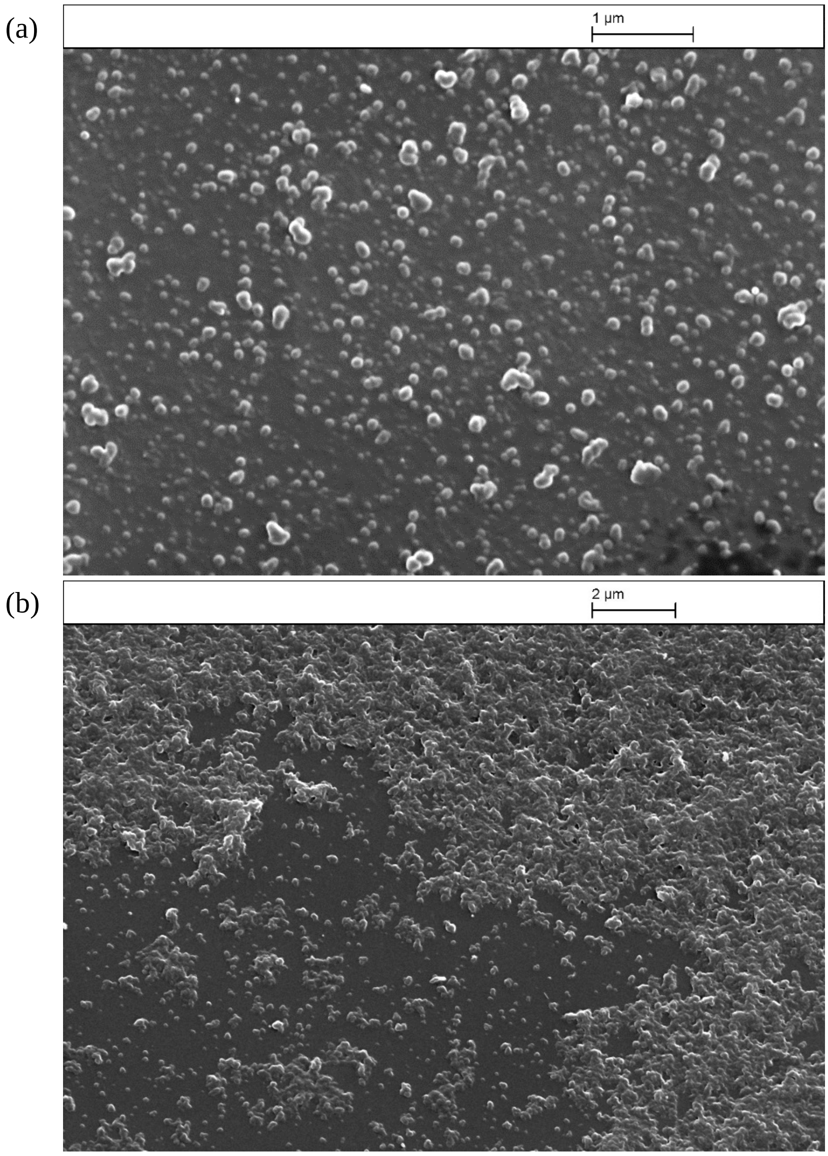


Figure 4. Variation of zeta potential with x_{PSSNa} for aqueous PEC dispersions prepared from 0.1 g L^{-1} individual PEL solutions for freshly prepared dispersions (unfilled circles) and 20 days after preparation (filled circles).

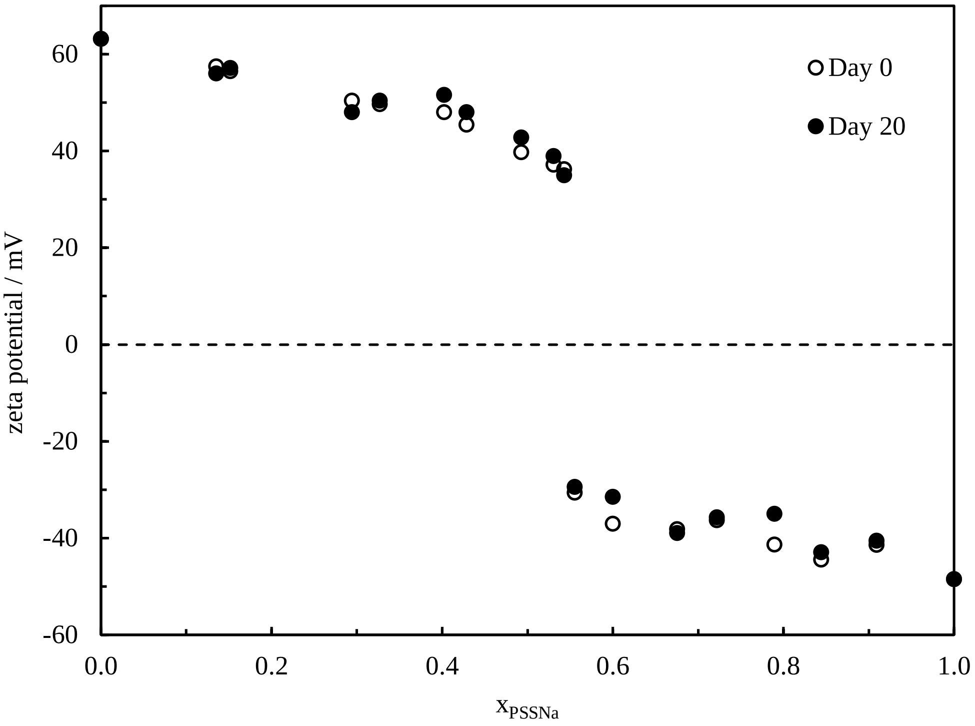


Figure 5. (a) Appearance of freshly prepared aqueous PEC dispersions prepared from 0.5 g L^{-1} individual PEL solutions at different x_{PSSNa} (given). Scale bar = 1 cm. (b) Transmittance at $\lambda = 400$ nm for the above.

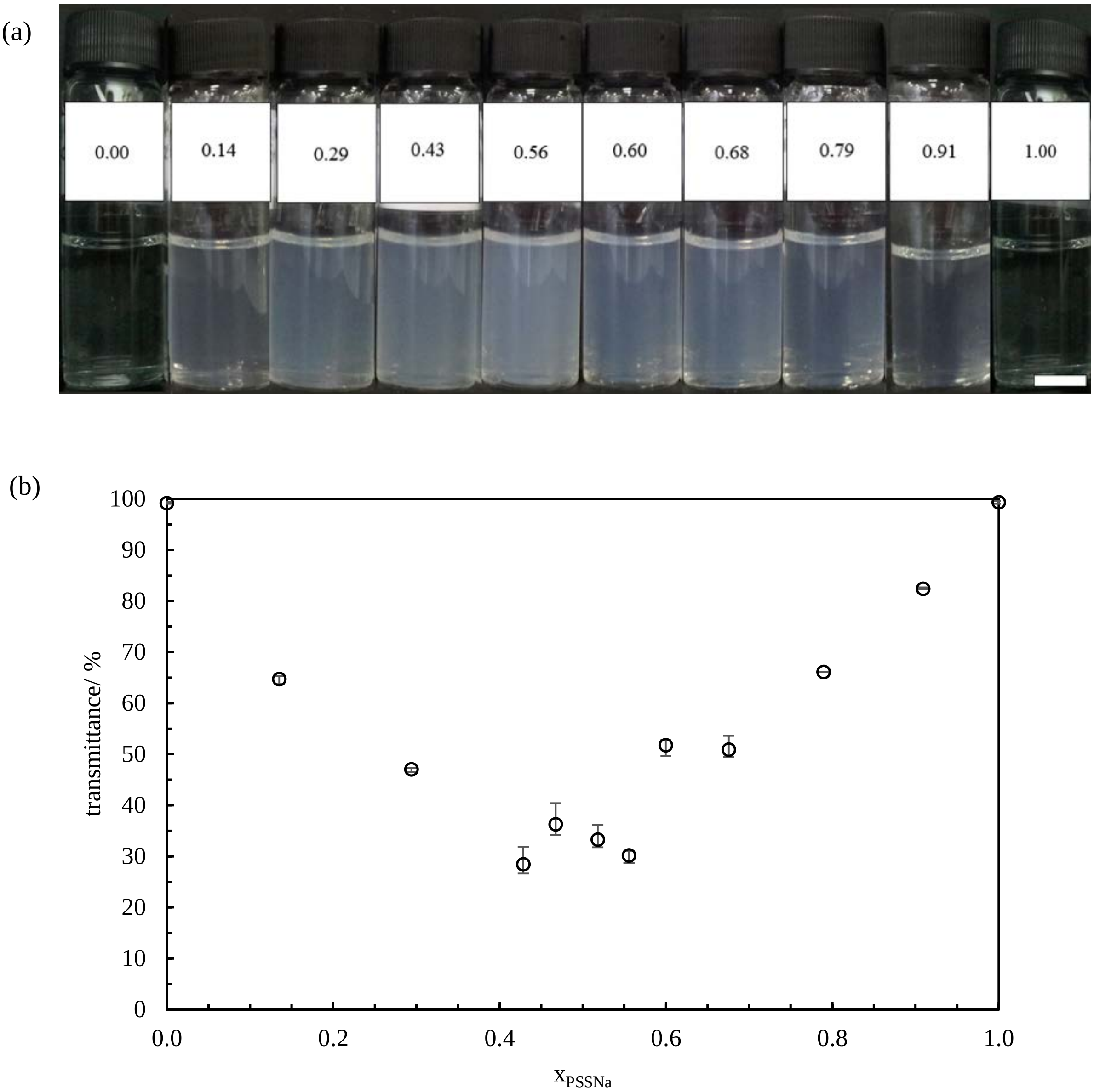


Figure 6. (a) Appearance of aqueous PEC dispersions (x_{PSSNa} ≈ 0.54) obtained from the individual PEL solutions of the given concentrations. Scale bar = 1 cm. (b) Average particle diameter (unfilled circles) and PDI (filled circles) *versus* [PSSNa] for the above.

(a)

(b)

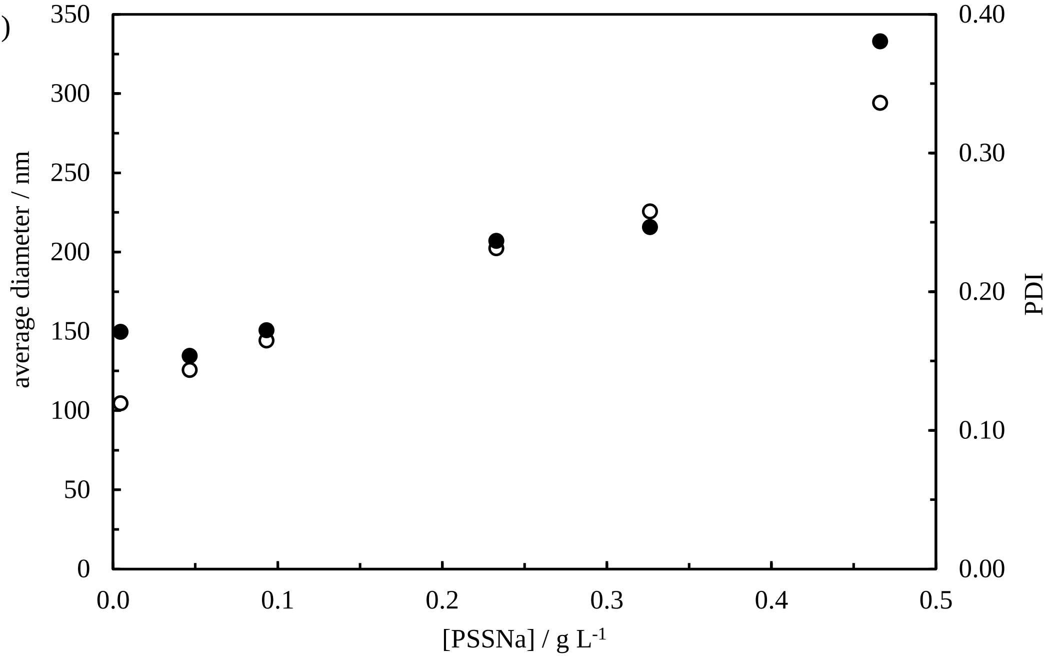


Figure 7. (a) Appearance of dodecane-in-water emulsions (ϕ_o = 0.2) stabilised by PEC particles prepared from 20 g L^{-1} individual PEL solutions at different x_{PSSNa} given. Scale bar = 1 cm. (b) Fraction of water (filled points) and fraction of oil (unfilled points) released from emulsions after 1 week *versus* x_{PSSNa}. (c) Average droplet diameter of above emulsions after preparation *versus* x_{PSSNa}.

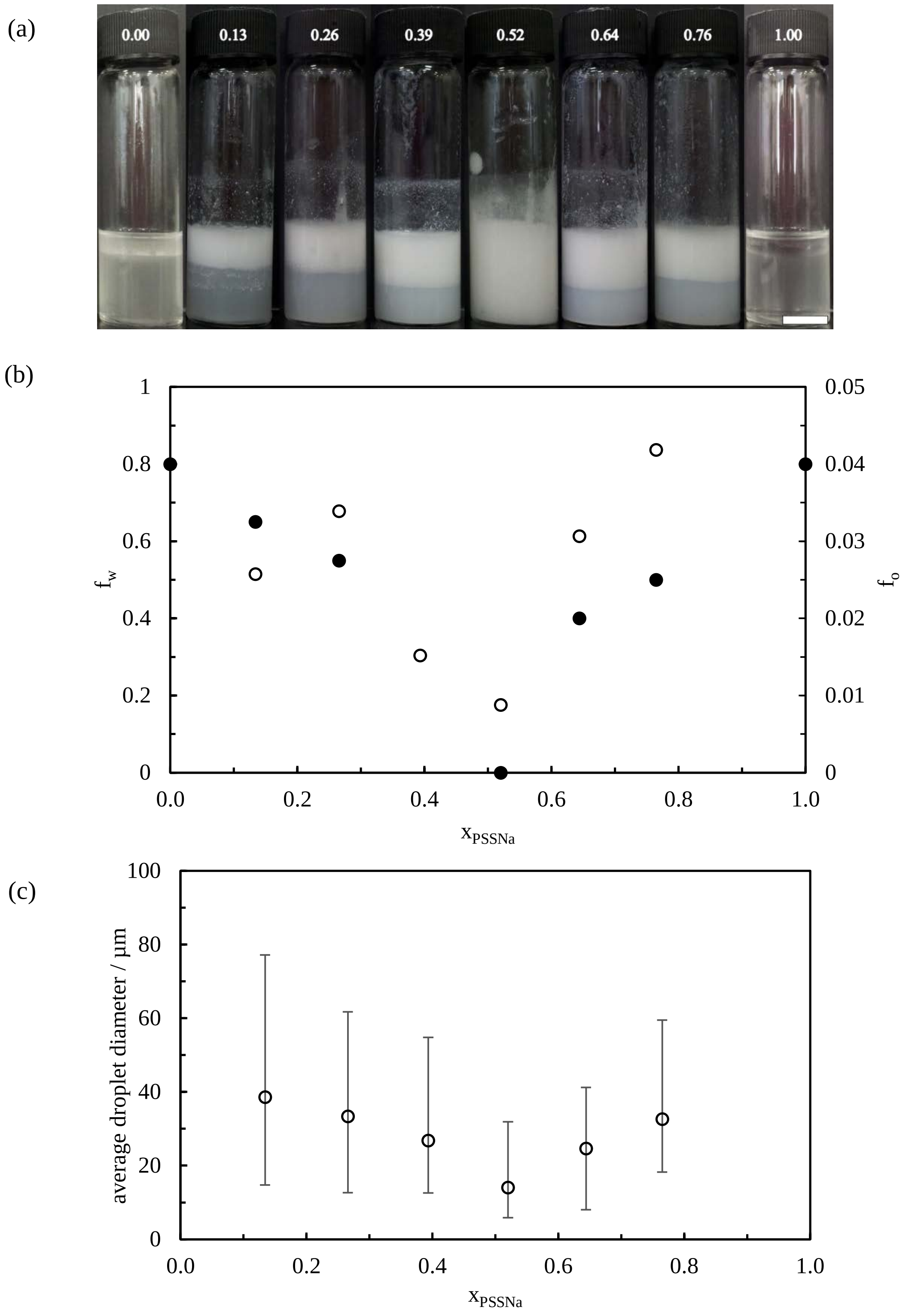


Figure 8. Optical microscope images of selected emulsions in Figure 7 at x_{PSSNa} of (a) 0.13, (b) 0.52 and (c) 0.64. The bare patches in (b) correspond to the glass slide.

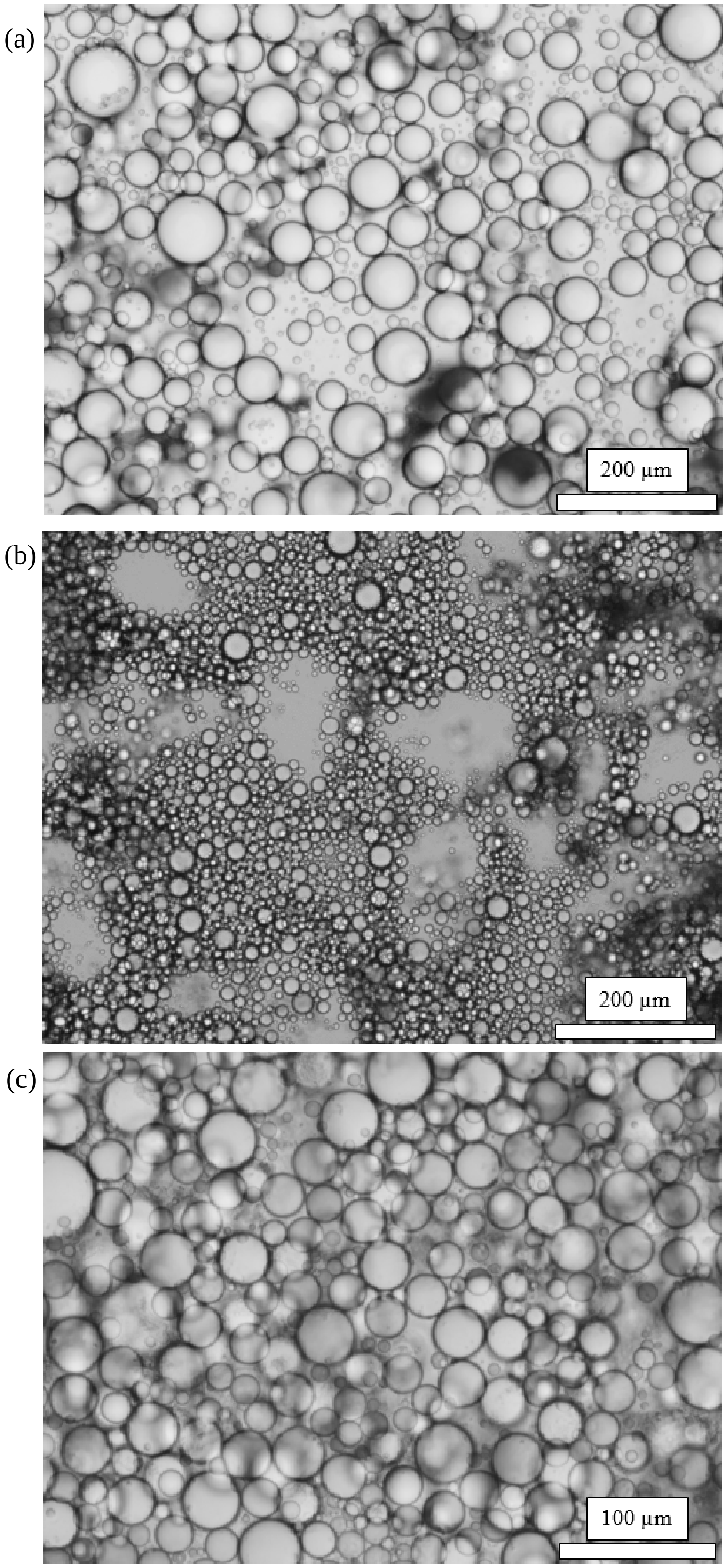


Figure 9. (a) Appearance of dodecane-in-water emulsions (ϕ_o = 0.2) stabilised by PEC particles (x_{PSSNa} ≈ 0.50) prepared from the individual PEL solutions of the given concentrations immediately after preparation. Scale bar = 1 cm. (b) Average droplet diameter *versus* initial [PSSNa] in water for the above emulsions. Inset - inverse of average droplet diameter as a function of initial [PSSNa] in water.

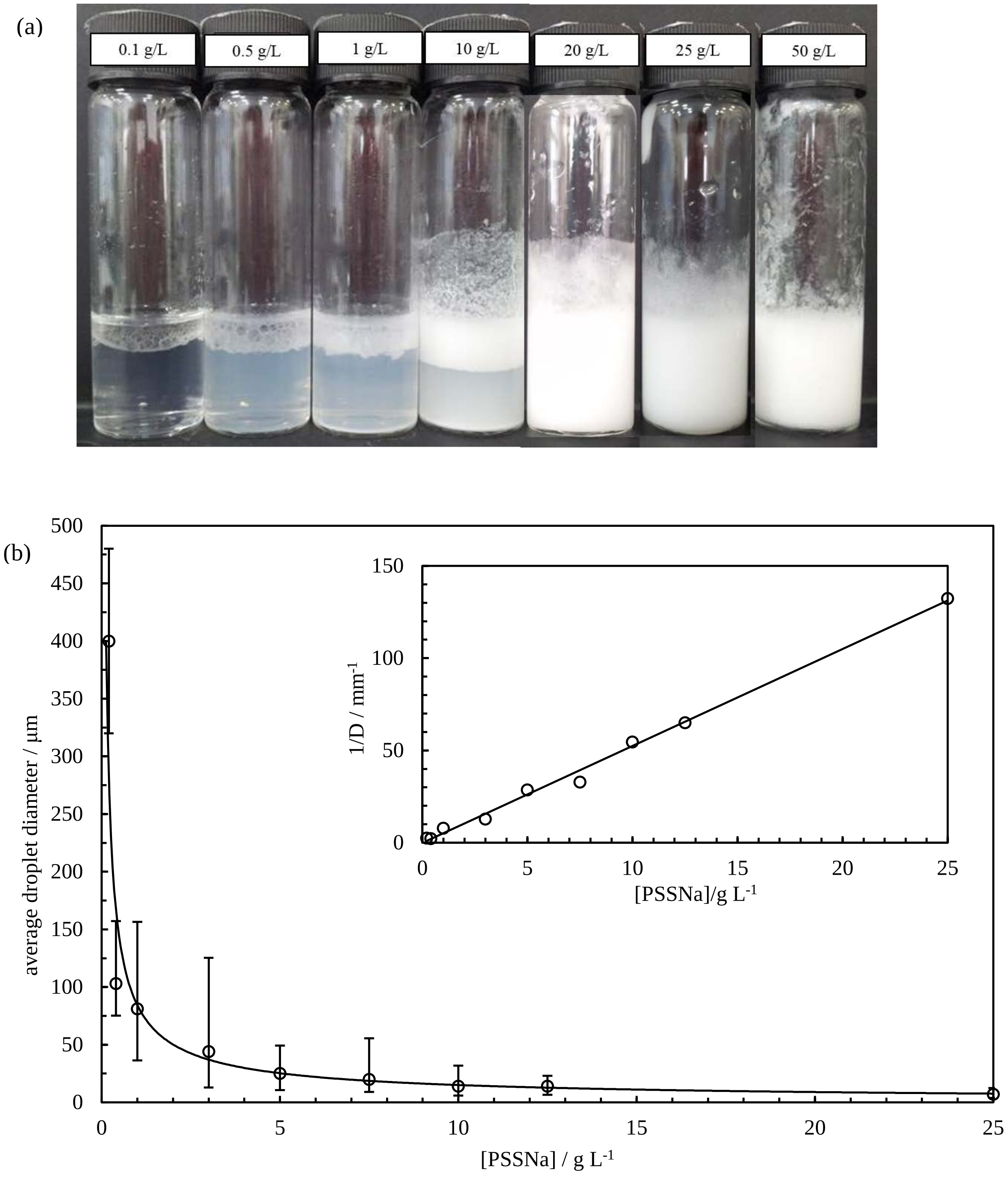


Figure 10. Cryo-SEM images of selected emulsions in Figure 9 for (a) 1 g L^{-1} PEL, x_{PSSNa} = 0.47 and (b), (c) 25 g L^{-1} PEL, x_{PSSNa} = 0.52.

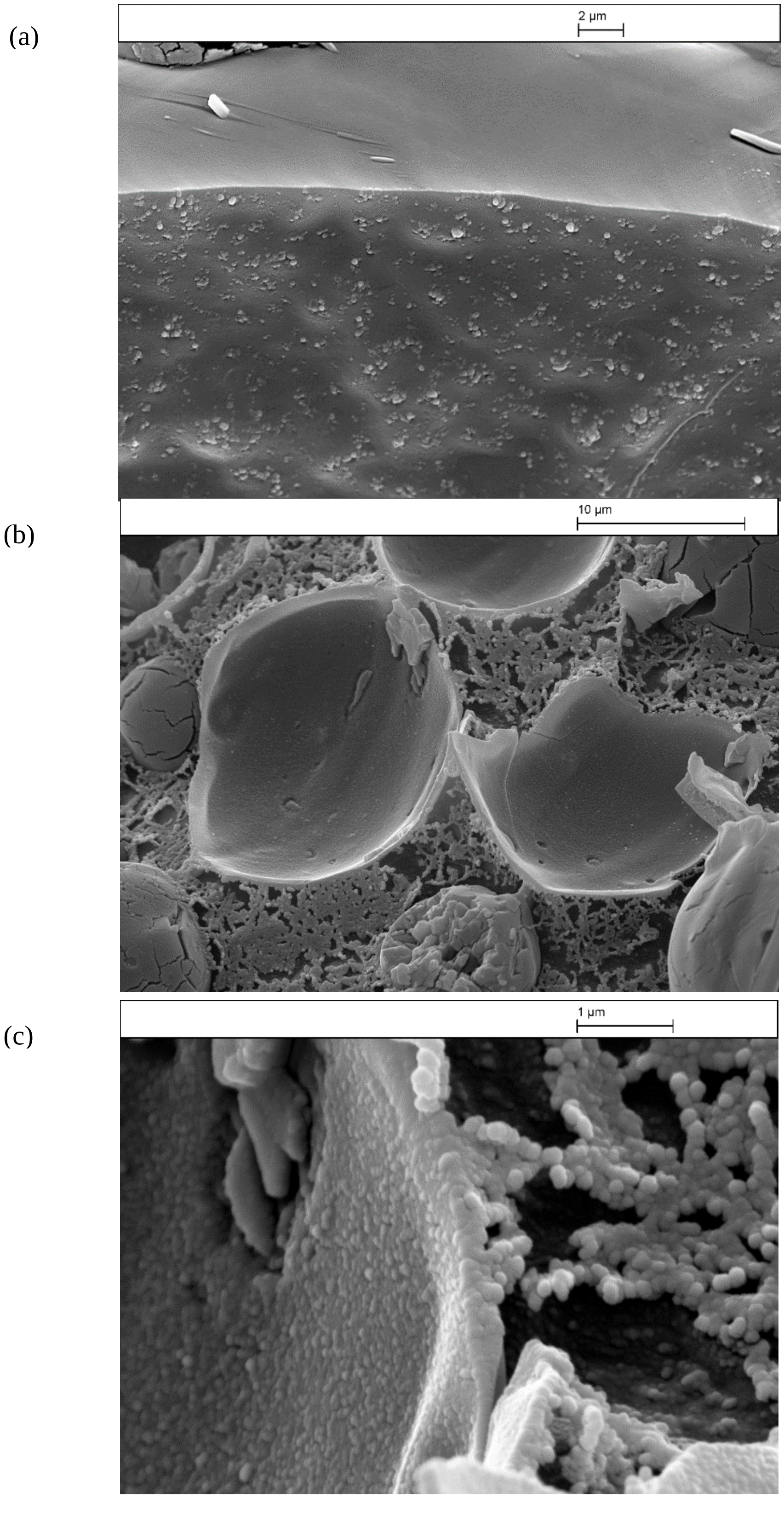


Figure 11. Appearance of dodecane-in-water emulsions immediately after preparation for different ϕ_o values (given). [PSSNa] in each emulsion is 8 g L^{-1} and x_{PSSNa} is 0.54. Scale bar = 1 cm.

Figure 12. (a) Appearance of aqueous PEC dispersions prepared from 1 g L^{-1} individual PEL solutions and x_{PSSNa} = 0.52 at different concentrations of NaCl (given) after preparation. (b) Appearance of dodecane-water emulsions (ϕ_o = 0.2) prepared from the dispersions in (a). Scale bar = 1 cm.

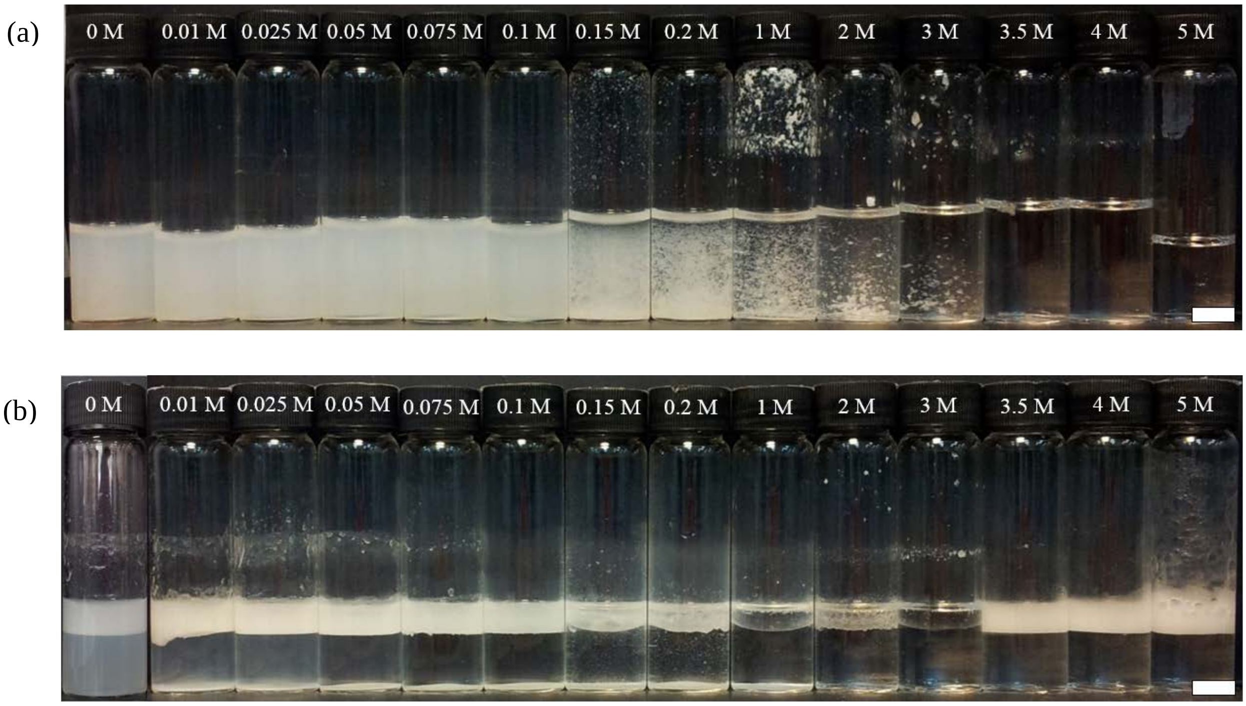


Figure 13. (a) Optical microscope images of dodecane-in-water emulsions (ϕ_o = 0.2) stabilised by PEC particles prepared from 1 g L^{-1} individual PEL solutions at different [NaCl] concentrations (from left to right and up to down): 0, 0.025, 0.05, 0.1, 4 and 5 M. (b) Average droplet diameter *versus* [NaCl] for emulsions in (a).

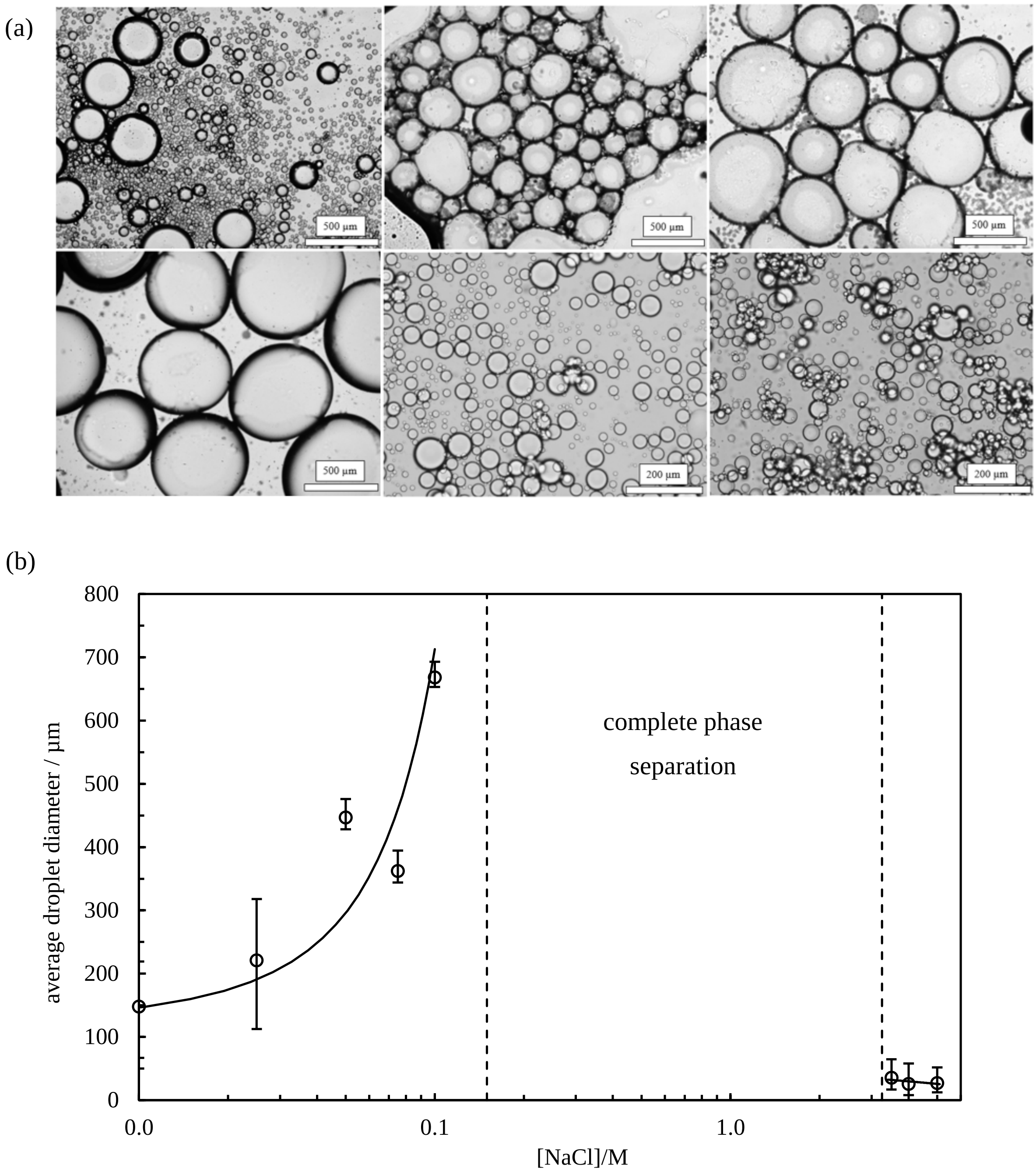


Figure 14. (a) Appearance of o/w emulsions of an aqueous PEC dispersion (50 g L^{-1} individual PEL solutions) and different oils (ϕ_o = 0.2) three months after preparation. (1) squalane, (2) isopropyl myristate, (3) toluene, (4) 50 cS PDMS and (5) liquid paraffin. (b) Corresponding optical micrographs for the above emulsions.

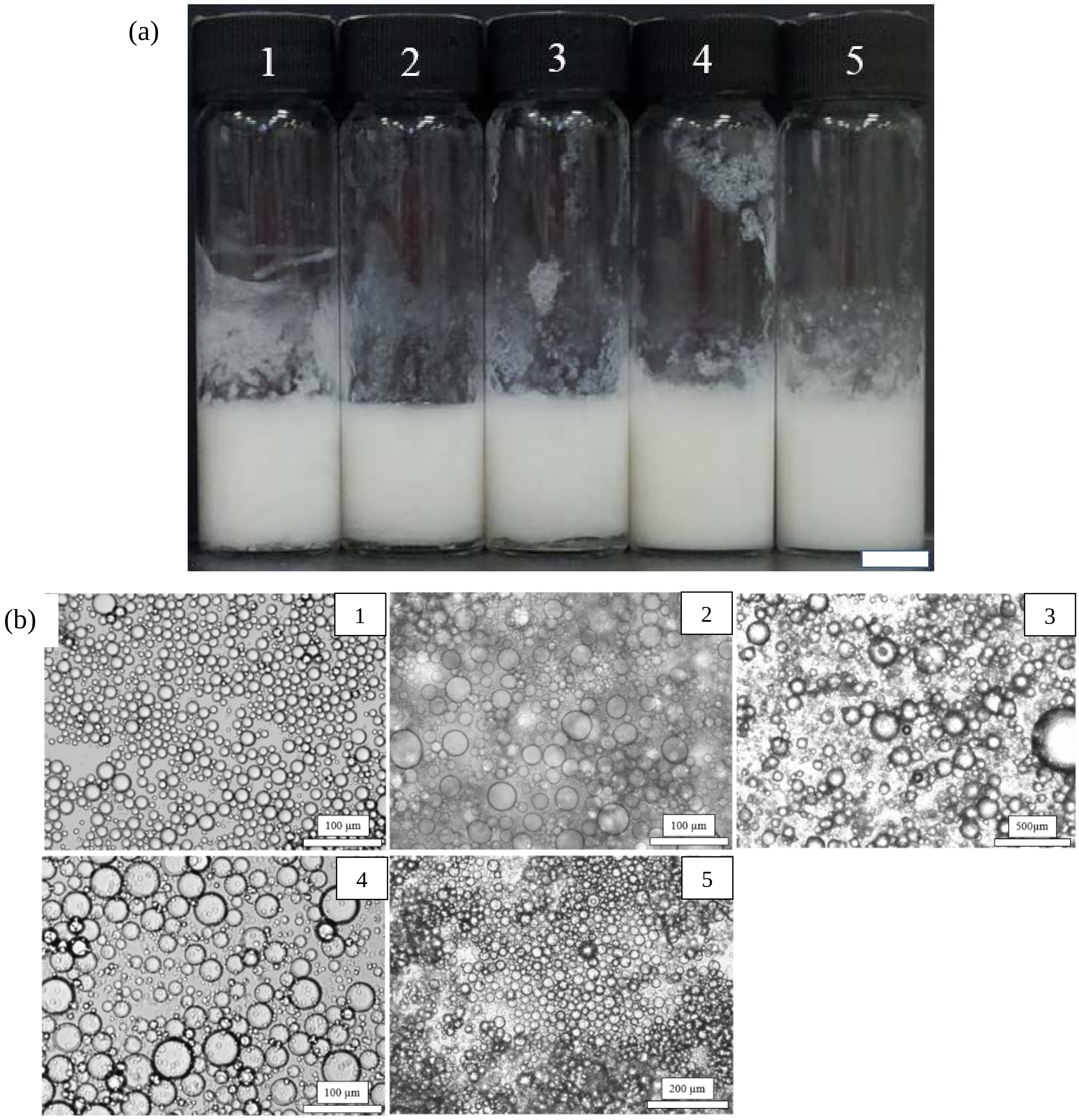


Figure 15. (a) Air-water surface tension *versus* x_{PSSNa} for PEC aqueous dispersions prepared from 0.5 g L^{-1} individual PEL solutions; dashed line is bare surface. (b) Dodecane-water interfacial tension *versus* x_{PSSNa} for PEC dispersions prepared from 1 g L^{-1} individual PEL solutions; dashed line is bare interface.