

ABSTRACT

In this work, association phenomena in aqueous systems containing (i) mixtures of polyelectrolyte and oppositely charged surfactant, and (ii) self-associating polymers were studied by means of scattering techniques.

First, mixtures of poly(styrenesulfonate anion), PSS^- , cetyltrimethylammonium cation, CTA^+ , and water were investigated in concentrated regime by small angle X-ray scattering and structures of phases were determined. A detail ternary phase diagram was outlined. It was shown that the hydrophobic interaction of the polyion styrene groups with the hydrophobic interior of surfactant aggregates has a significant effect on phase behavior and structures. Only the ordered hexagonal and disordered micellar phases were detected; no cubic phase was found. The general conclusions are that (i) the hydrophobic interaction promotes dissolution of the CTAPSS complex salt when the polyion salt is added and provides further stabilization of the dense hexagonal phase when the surfactant salt is added and that (ii) the addition of the polyelectrolyte induces associative phase separation and phase inversion, whereas the addition of surfactant leads mainly to segregative phase separation.

Polyelectrolyte-surfactant complexes of NaPSS with cetylpyridinium chloride, CPC, were investigated in 0.1 M NaCl in the dilute regime by dynamic and static light scattering for a broad range of surfactant cation, CP^+ , to polyion, PSS^- , charge ratios, S/P . NaPSS samples with rather different molar mass values were used, denoted as NaPSS-l and NaPSS-h. The precipitation of the CPPSS complex starts at around $S/P = 0.72$, irrespective of the polyion chain length. This is attributed to the specific hydrophobic interaction between the benzene groups on the polyion and the surfactant micelle, which leads to less efficient screening of the polyion charge. In contrast, the polyion chain length has a pronounced effect on the redissolution with excess surfactant and on structural properties of the CPPSS complex. The CPPSS-l complexes redissolve at $S/P \approx 240$, the aggregates are small and dense, their shape is close to spherical. On the other hand, the CPPSS-h complexes require a much higher surfactant excess to achieve re-dissolution ($S/P \approx 2400$), have no well-defined structure and reveal a stronger tendency toward intermolecular association.

Solutions of isotactic, iPMA, and atactic, aPMA, poly(methacrylic acid) in water, in the presence 0.1 M LiCl, NaCl, and CsCl, were investigated by dynamic and static light scattering in dependence on degree of neutralization, α_N , of carboxyl groups. The results show that both PMA isomers, irrespective of the present monovalent salt, are intermolecularly associated at low degrees of neutralization ($\alpha_N = 0$ for aPMA and $\alpha_N \approx 0.25$ for iPMA). The aggregates have characteristics of microgel particles. According to the values of the shape parameter ρ (≈ 0.6 and 0.75 for iPMA and aPMA, respectively, regardless of the counterion) iPMA aggregates have a more compact and denser structure than aPMA ones. At higher α_N ($\alpha_N \geq 0.25$ for aPMA and $\alpha_N \geq 0.4$ for iPMA), the slow diffusion corresponding to multimacroion domain formation (so-called polyelectrolyte effect) is observed for both PMAs. It was identified for all $\alpha_N \geq 0.4$ with iPMA, irrespective of the counterion, whereas with aPMA it was detected only for $\alpha_N = 1$

in the presence of NaCl. These results suggest a comparatively higher polyion charge of the isotactic chain. Furthermore, the effect of shear on intermolecular association was followed for both isomer forms in the presence of 0.1 M NaCl. The results showed that aggregates of aPMA multiply as a result of mechanical stress and gradually decrease in number after its cessation (phenomenon called negative thixotropy), whereas those of the highly regular iPMA are disrupted by shear and gradually reform in solution at rest, which indicates the absence of negative thixotropy.

In addition, the effect of NaCl concentration, c_s , on intermolecular association and on the polyelectrolyte effect for both PMAs was investigated. The results demonstrate that for aPMA c_s has a major effect on both phenomena. The size and shape of aPMA aggregates at $\alpha_N = 0$ initially steeply increases with increasing c_s , reaches a maximum at around $c_s = 0.07$ M ($\rho \approx 0.8$) and thereafter gradually decreases. The reason for such peculiar behavior is attributed to competition of self-ionization process and electrostatic screening effect of NaCl. The polyelectrolyte effect in aPMA solutions is the most pronounced at $\alpha_N = 1$, where it was observed up to 0.1 M NaCl, and disappears at lower c_s with decreasing α_N . Differently, the size of iPMA aggregates at $\alpha_N \approx 0.25$ increases with increasing c_s , whereas their shape parameter is constant ($\rho \approx 0.6$) in the whole c_s range.

Keywords: polyelectrolyte-surfactant mixtures, isotactic and atactic poly(methacrylic acid), associating polyelectrolytes, intermolecular association, scattering methods.

POVZETEK

V pričujočem delu sem z metodami sipanja svetlobe proučevala asociacijske pojave v vodnih sistemih, ki vsebujejo (i) mešanice polielektrolita in nasprotno nabite površinsko aktivne snovi, PAS, in (ii) asociirajoče polielektrolite.

Najprej sem v mešanicah polistirensulfonatnega aniona, PSS⁻, cetiltrimetilamonijevega kationa, CTA⁺, in vode določila fazni diagram. Pripravila sem kompleksno sol med polianionom in kationom PAS, označeno kot CTAPSS, in jo mešala bodisi s polielektrolitom bodisi s PAS in vodo. Z metodo ozkokotnega sipanja rentgenske svetlobe sem določila strukture posameznih faz v ravnotežju, ter njihove sestave in skonstruirala fazni diagram na tako imenovani polielektrolitski in surfaktantni ploskvi. Bistvena ugotovitev te študije je, da ima specifična hidrofobna interakcija med benzensulfonsko skupino na poliionu in hidrofobno notranjostjo micela PAS pomemben vpliv na fazno obnašanje in na strukture, ki se tvorijo. Opazila sem le heksagonalno in micelno strukturo, ne pa tudi kubične, ki so jo raziskovalci opazili v podobnem sistem s hidrofilnim polielektrolitom (poliakrilatnim anionom), kjer do omenjene specifične interakcije ne pride. Omenjena specifična interakcija je tudi vzrok za dobro topnost kompleksne soli CTAPSS v raztopinah z dodatkom polielektrolita in za dodatno stabilizacijo kompleksne soli (goste heksagonalne faze) ob dodatku PAS.

Z metodami dinamičnega, DLS, in statičnega sipanje svetlobe, SLS, sem raziskovala tudi molekulske značilnosti topnih kompleksov med cetilpiridinijevim kloridom, CPC, in natrijevim polistirenesulfonom, NaPSS, v vodnih raztopinah s koncentracijo enostavne soli NaCl 0.1 M. Komplekse med NaPSS in CPC sem označila kot CPPSS. Meritve sem opravila v širokem območju molskega razmerja, S/P , med CPC in NaPSS. Uporabila sem dva vzorca NaPSS z različno molsko maso (različno dolžino verige poliiona), da bi ugotovila, kakšen je vpliv dolžine verige poliiona na obnašanje kompleksov. Obarvanje kompleksne soli CPPSS se, ne glede na dolžino verige poliiona, začne pri razmerju $S/P \approx 0.72$, kar je precej višje kot v poprej omenjenih mešanicah s poliakrilatnim anionom. Tudi to sem pripisala specifični hidrofobni interakciji med benzenskimi skupinami na poliionu in micelami PAS, ki vodi do manj učinkovitega senčenja naboja na poliionu in zato do boljše topnosti kompleksne soli, ne glede na njegovo dolžino. Nasprotno pa ima dolžina verige poliiona močan vpliv na ponovno raztopitev (angl. *redissolution*) oborjenega kompleksa, ki jo dosežemo z dodatkom presežne PAS. Vrednost S/P za ponovno raztopitev je okrog 240 za kratke verige in okrog 2400 za dolge verige. Ponovno raztapljanje je dokaj dolgotrajen proces: za raztopitev kompleksov s kratkimi verigami je potrebno nekaj dni, za komplekse z dolgimi verigami pa celo več tednov. To opažanje razložimo z entropijo mešanja, ki je v prvem primeru dosti bolj pozitivna.

V drugem delu sem z metodami DLS in SLS raziskovala obnašanje vodnih raztopin dveh stereoizomer polimetakrilne kisline, izotaktične, iPMA, in ataktične, aPMA, v prisotnosti alkalijjskih kloridov LiCl, CsCl

in NaCl. Spreminjala sem stopnjo nevtralizacije karboksilnih skupin, α_N , na PMA in tudi koncentracijo elektrolita (NaCl). Medtem ko je aPMA v vodi topna ne glede na vrednost α_N , se iPMA raztopi šele nad $\alpha_N \approx 0.20$. Rezultati so pokazali, da pri obeh oblikah PMA, ne glede na prisoten protiion (Li^+ , Na^+ ali Cs^+), pri nizkih α_N ($\alpha_N = 0$ za aPMA in $\alpha_N \approx 0.25$ za iPMA) pride do medmolekulske asociacije, ki je precej obsežnejša v primeru iPMA. Nastali agregati imajo lastnosti mikrogelov z večjo gostoto v sredini in manjšo na površini agregata. Glede na vrednosti parametra oblike, ρ (≈ 0.6 za iPMA in ≈ 0.75 za aPMA, ne glede na protiion) imajo agregati med verigami iPMA bolj kompaktno in gosto strukturo kot agregati med verigami aPMA. To sem pripisala bolj učinkoviti tvorbi vodikovih vezi med verigami izotaktičnega polimera in večji hidrofobnosti verig, kar je posledica urejenosti na molekularnem nivoju.

Pri višjih α_N ($\alpha_N \geq 0.25$ za aPMA in $\alpha_N \geq 0.4$ za iPMA) do agregacije ne pride, pojavi pa se t.i. počasna difuzija, ki je posledica polielektrolitskega efekta. Pri meritvah DLS sem opazila dodaten difuzijski proces z majhnim difuzijskim koeficientom, ki je posledica tvorbe "domen" med polioni zaradi elektrostatskega odboja med nabitimi verigami (da gre za neke vrste korelirano gibanje nabitih verig). Počasno difuzijo sem v primeru iPMA opazila za vse $\alpha_N \geq 0.4$, ne glede na prisoten protiion, medtem ko je bila v primeru aPMA opažena le pri $\alpha_N = 1$ v prisotnosti Na^+ ionov. Ti rezultati kažejo na višji učinkoviti naboj izotaktičnega poliona.

Za obe stereoizomerni obliki PMA v 0.1 M NaCl sem zasledovala tudi vpliv strižne obremenitve na medmolekulsko asociacijo. Rezultati kažejo, da se pod vplivom strižne obremenitve število agregatov med verigami aPMA poveča, vendar pa po prenehanju delovanja strižnih sil njihovo število postopoma upade. To opažanje sem razložila s pojavom negativne tiksotropije (antitiksotropije). Nasprotno pa se pod vplivom strižne obremenitve agregati med verigami iPMA razgradijo, po njenem prenehanju pa se postopoma spet tvorijo, kar je ravno nasprotno kot pri aPMA. Odstotnost negativne tiksotropije pri iPMA sem razložila z veliko osnovno težnjo izotaktične verige po asociaciji in njeno večjo togostjo.

Ključne besede: mešanice polielektrolitov in površinsko aktivnih snovi, izotaktična in ataktična polimetakrilna kislina, asociirajoči polielektroliti, medmolekulska asociacija, sipanje svetlobe.