Phase behavior of polymer-surfactant systems in relation to polymer-polymer and surfactant-surfactant mixtures

Björn Lindman, Ali Khan, Eduardo Marques*, Maria da Graca Miguel*, Lennart Piculell and Kyrre Thalberg#

Physical Chemistry 1, Chemical Center, University of Lund, P O B 124, S-221 00 Lund, Sweden
* Permanent address: Department of Chemistry, University of Coimbra, Portugal
# Present address: Astra Draco, P O B 34, S-221 00 Lund, Sweden

Abstract - Novel phase diagrams of systems of water and two cosolutes of colloidal size, either macromolecules or surfactant micelles, are presented. For a mixture of two oppositely charged surfactants, a complex phase diagram is obtained with several liquid crystalline phases and equilibrium vesicles. There is a strong tendency for two surfactants to mix and form a range of structures governed by geometrical packing and electrostatic interactions. In recent years, surfactant self-assembly in the presence of different polymers has attracted a great interest, both from fundamental and applied aspects. Attractive or repulsive interactions are observed depending on the system. For the former case, dilute solutions may be analysed in terms of a binding of the surfactant to the polymer or a depression of the critical micelle concentration of the surfactant by the polymer. An important feature of these solutions is thus that the surfactant molecules, also when interacting intimately with a polymer, give micellar-type structures. The phase behavior of polymer-surfactant systems has only recently attracted greater attention but has been shown most significant for the understanding of the interactions involved. Different types of phase separation phenomena are encountered including segregative and associative types. For systems of a polyelectrolyte and an oppositely charged surfactant, an associative interaction is observed leading to phase separation into one solution concentrated in both polymer and surfactant and one very dilute solution. In the presence of an electrolyte, phase separation may be eliminated and, at higher concentrations, a polymer incompatibility type of phase separation may result. It is found fruitful to analyse the phase diagrams of polymer-surfactant systems with those of polymer-polymer and surfactant-surfactant mixtures as a basis. Analogies and differences are discussed and it is found that polymer-surfactant systems show basic similarities to polymer-polymer systems, while surfactant mixtures are different, which is due to the exchange of surfactant molecules between micelles and the formation of mixed micelles and other aggregates. Surfactant mixtures are, therefore, not displaying a segregative type of phase separation.

INTRODUCTION

Polymer-surfactant solutions have been intensely studied during recent years (ref. 1-4), mainly with respect to aggregation phenomena in relatively dilute systems and rheological properties. Phase diagrams give fundamental information on the solute-solute interactions and have been obtained for a number of cases and it was suggested that the phase behavior for polymer-polymer and surfactant-surfactant systems should provide an appropriate starting point for analysing the rather complex patterns observed for polymer-surfactant systems (ref. 5).

In this treatise, we will review some of our recent findings for two systems of oppositely charged cosolutes, one polymer-surfactant and one surfactant-surfactant system. We will compare those with observations in the literature for analogous systems as well as for polymer-polymer solutions. Thereafter, we will consider more generally the problem of phase separation in solutions containing two types of molecules or self-assemblies of colloidal dimensions. It will be fruitful to distinguish between segregative and associative phase separation phenomena and examples are provided for the different types from studies on the solutions mentioned. It will be demonstrated that polymer-surfactant solutions show many analogies with mixed polymer solutions, while similarities with mixed surfactant systems are less apparent.

A MIXTURE OF A CATIONIC AND AN ANIONIC MIXTURE

Mixed cationic-anionic surfactant systems have been studied during a long period of time (ref. 6-13), partly due to their relevance for a large number of applications, but more complete phase diagrams have in general not been obtained. One reason for this is the complex nature, as these systems must be treated as four-component systems requiring a three-dimensional representation at constant T and p.

In recent years, Kaler and coworkers (ref. 7, 14) have provided more detailed studies of the phase behavior of a number of mixtures of single alkyl chain cationic and anionic surfactants, with interesting observations including that of spontaneously forming, and apparently thermodynamically stable, vesicles.
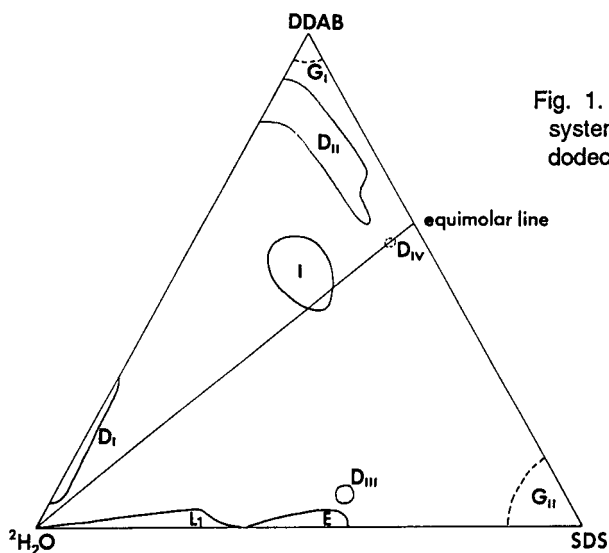

Fig. 1. Schematic (pseudo-) ternary phase diagram of the system of didodecyldimethylammonium bromide, sodium dodecyl sulfate and water at 40 °C.

In Fig. 1 we show the preliminary phase diagram for a system of a double-chain cationic surfactant and a single chain anionic surfactant, that has been studied in our laboratory (ref. 22). We note the complexity of the phase equilibria -many aspects of which remain to be studied- and, in particular, the presence of several regions of lamellar liquid crystalline phase (D) and the appearence of novel phases along the equimolar line. Also in this system there are equilibrium vesicles, enriched in either surfactant, forming for dilute solutions. The sequence of phases found on changing the mixing ratio follows from simple geometric packing (ref. 15, 16) and electrostatic considerations (ref. 17, 18). So, for example, sodium dodecyl sulfate micelles (L_1) grow on introduction of the oppositely charged cationic surfactant and the hexagonal phase (E) is transformed into a lamellar one. An unusually large region of bicontinuous cubic liquid crystalline phase (I) is found; the cubic phase appears to be able to coexist with at least four different lamellar phases. The cationic surfactant forms two lamellar phases with water. The dilute one can incorporate only minute amounts of the anionic surfactant, while the uptake in the concentrated one is very large. This is probably related to the dominating role of long-range electrostatic forces for the stability of the dilute phase; the same difference in behavior between the two lamellar phases relates to the solubilisation of simple hydrocarbons (ref. 19).

In the earlier work of Jokela et al. (ref. 6, 20-21) on catanionic surfactants (i. e. surfactants composed of a cationic amphiphile ion and an anionic one with no small counterions), the equilibrium between a very dilute solution and a concentrated lamellar phase or, at a lower temperature, a solid crystalline phase was found to be a rather general feature. Analogous phase separation phenomena were noted in the studies on mixed cationic-anionic surfactant systems by Kaler et al. (ref. 7, 14) and Marques et al. (ref. 22).

A MIXTURE OF A CATIONIC SURFACTANT AND AN ANIONIC POLYMER

Adding an ionic surfactant to a solution of an oppositely charged polyelectrolyte in general leads to phase separation (often referred to as "precipitation" but this notion is not generally suitable) (ref. 1, 23-26). At higher additions of surfactant, phase separation may be eliminated and a homogeneous solution formed ("redissolution") and this effect is also produced by addition of simple electrolyte. In a pseudo-ternary representation of the phase diagram, as exemplified in Fig. 2, there is a two-phase region encircled by a homogeneous one-phase region (ref. 27). As can be seen from the direction of the tie-lines, phase separation results in one dilute solution in equilibrium with another phase (isotropic, often gel-like), which is concentrated in both cosolutes. The size of the two-phase region increases with the polymer molecular

Effect of salt on
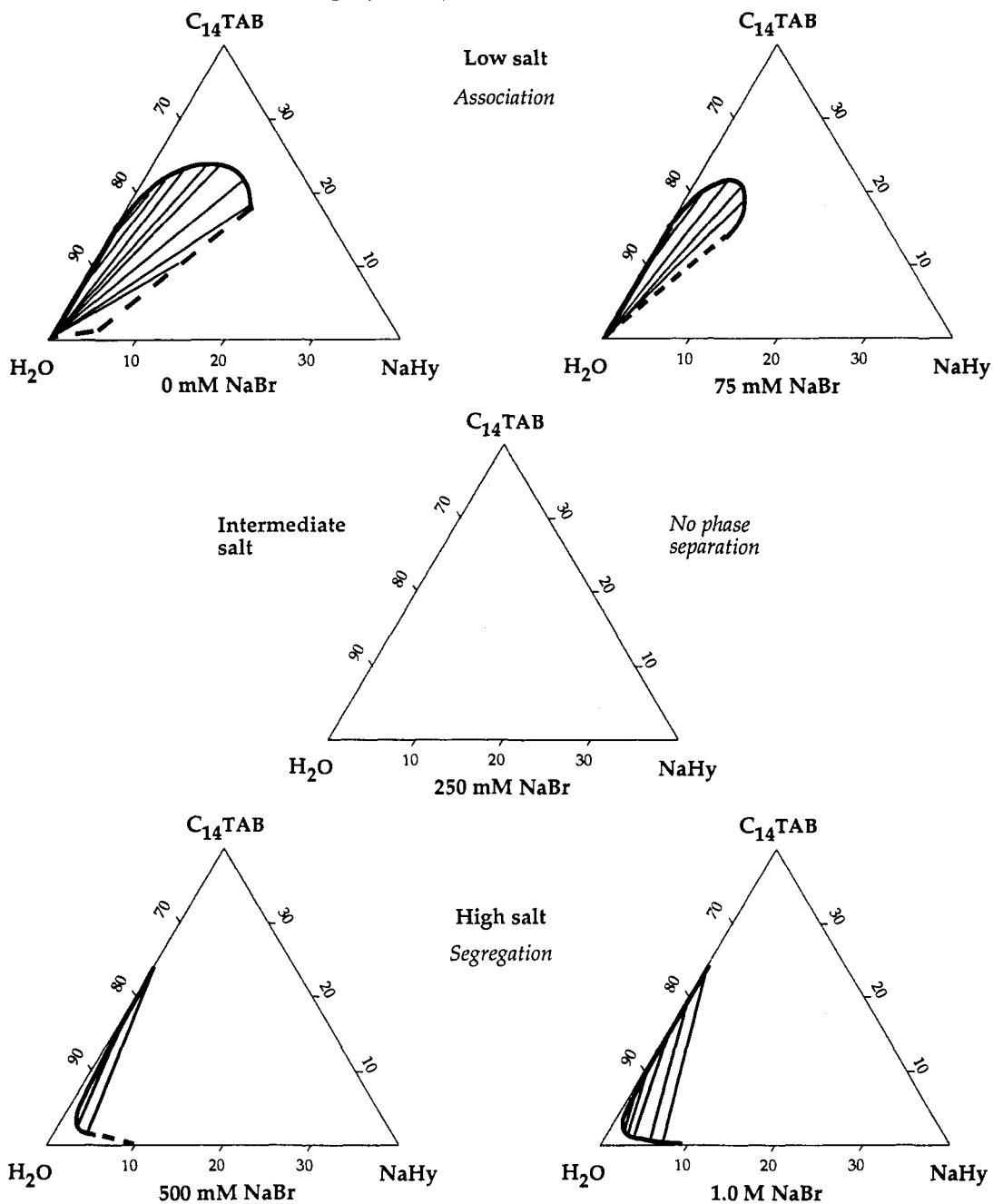## polyectrolyte + ionic surfactant

Fig. 2. Pseudo three-component phase diagrams for the system of sodium hyaluronate, tetradecyl-trimethylammonium bromide and water at different concentrations of added salt. (From ref. 5).

weight and with the alkyl chain length of the surfactant as well as with the charge density of the polyelectrolyte (ref. 3, 27-30).

Salt addition to these systems fundamentally changes the phase separation pattern (Fig. 2). The two-phase region at first shrinks and then disappears at a certain electrolyte concentration, but at higher salt addition phase separation is again found. However, this phase separation is quite different in nature, and as can be seen from the direction of the tie-lines, coexisting phases are enriched in either of the two cosolutes.

MIXTURES OF TWO OPPOSITELY CHARGED POLYMERS

This type of systems has been studied quite extensively (ref. 31) and detailed investigations of the ternary phase diagrams of such mixtures and their dependences on the concentration of added electrolyte and the linear charge densities of the two polyelectrolytes have been presented in recent years (ref. 32-33). The dominating feature of these systems is a strong tendency towards phase separation into one phase concentrated in both polymers and one dilute solution, and the phase diagram is analogous to that described above for a mixture of a polyelectrolyte and an oppositely charged surfactant.

On addition of salt, there is in general an increase in miscibility and in many cases the phase separation does not occur above a certain salt concentration. An interesting illustration of the salt dependence is offered by a study by Albertsson (ref. 34) on an aqueous mixture of dextran sulfate and diethylaminoethyldextran. The phase separation obtained in the absence of added salt disappears at a certain salt concentration and when more salt is added there is a separation into two polymer solutions, enriched in the two cosolutes, i. e. a phase behavior similar to that showed in Fig. 2 for a polymer-surfactant mixture.

GENERAL ASPECTS OF PHASE SEPARATION IN MIXED MACROMOLECULAR SOLUTIONS

The phase separation observed for the three types of systems examined above show for the salt-free case one fundamental similarity in that there may be a phase separation into one dilute solution phase and one phase concentrated in both cosolutes. Since the two cosolutes tend to assemble in the same concentrated phase, we will term this an associative type phase separation.

As a consequence of the small contribution from the translational entropy of mixing for macromolecular solutes, mixtures of two polymers in solution have a strong tendency to phase separate. The typical phase separation is not, however, of the associative type. Instead, the two polymers normally tend to concentrate in two different solution phases ("polymer incompatibility"), since interpolymer interactions normally are repulsive. As in ref. 5, we will here denote the latter type of phase separation as segregative. Schematic phase diagrams for the two types of behavior are depicted in Fig 3. For weak attractive interactions, homogeneous mixing is predicted while the associative phase separation pertains to strong attractive interactions, such as for two oppositely charged polymers in water without added salt. In either case of phase separation, an increased polymer molecular weight will lead to an increased tendency to phase separation.
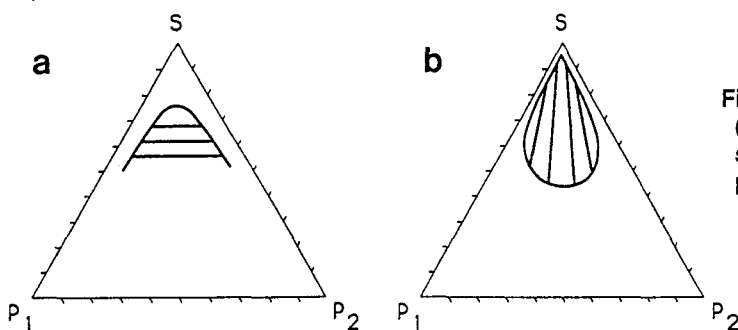

Fig. 3. Segregative (a) and associative (b) phase separation in mixed polymer solutions. S denotes solvent and P polymer. (From ref. 5).

The association of two oppositely charged polymers is primarily an entropic effect (ref. 31) and to understand its origin we must consider the inhomogeneous distribution of the counterions in a salt-free polyelectrolyte solution, with a marked enrichment owing to the attractive Coulomb effect near a highly charged polyion. The non-uniform counterion distribution corresponds to a loss of entropy relative to the case of a completely homogeneous distribution. Introducing an oppositely charged polymer with its counterions, a more uniform counterion distribution can be obtained by letting the two charged polymers associate. The release of the counterion atmospheres around the polyions gives rise to an increase in entropy. This entropy increase is reduced on the addition of salt, since salt addition creates a more homogeneous counterion distribution for the two polyions, which explains the decreased tendency to association. The formation of a one-phase region on addition of salt is, however, only expected when the two polymers are intrinsically soluble and do not owe their solubility to the dissociation of the counterions.

As already noted, the three types of systems, surfactant-surfactant, polymer-surfactant and polymer-polymer, show for the case of two oppositely charged cosolutes an important analogy in phase behavior, with an associative phase separation, which can be referred to a strongly attractive interaction. If this strong attraction is eliminated by addition of electrolyte, the phase diagram changes dramatically. For the polymer-

surfactant and polymer-polymer systems, there is a change over to a segregative type of phase separation at high salt- which is, however, only expected for an intrinsically segregating pair of cosolutes- but this is not observed for the mixed surfactant system. In fact this is just one example of a very general difference, observed for different classes of polymer and surfactant molecules, nonionic or ionic. Thus both polymer-surfactant and polymer-polymer systems show a great tendency to a segregative phase separation, while this has to our knowledge not been observed for surfactant-surfactant systems, even when there is a strongly repulsive interaction.

As an example, Shinoda and Kunieda (ref. 35) investigated the phase behavior of a mixture of two cationic surfactants, one single-chain and one double-chain. On increasing the fraction of double-chain surfactant, there is change from micellar solution, via hexagonal phase to lamellar phase, exactly as would be predicted from simple geometrical packing conditions for a single surfactant having a weigthed average geometry. On the other hand, the mixing of a polymer with a similarly charged surfactant (ref. 36-37) or of two similarly charged polymers (ref. 34, 38-39) has been observed to lead to a segregative type of phase separation, with or without added salt, as illustrated in Fig. 5 for a mixture of an anionic surfactant and an anioic polyion.
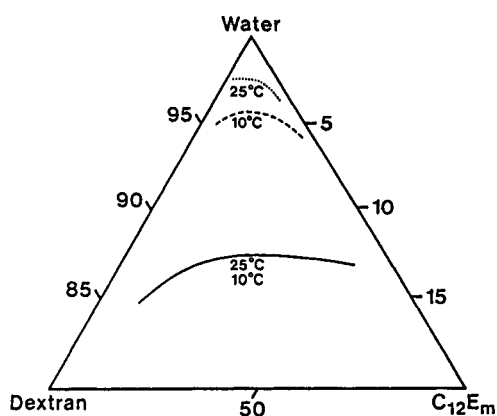

Fig. 4. Binodials for aqueous mixtures of dextran with the nonionic surfactant $C_{12}E_8$ at 10 °C or 25 °C (——; no significant temperature dependence was detected), or with $C_{12}E_5$ at 10 °C (---) or 25 °C (·····). (From ref. 5).
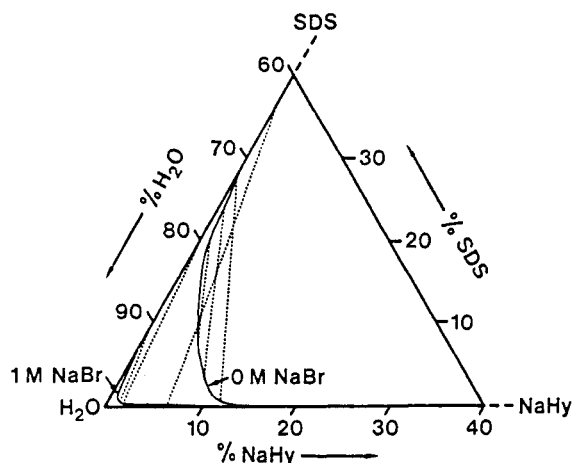
Fig. 5. Phase diagram for the system of sodium hyaluronate, sodium dodecyl sulfate and water at 40 °C without added salt and at addition of 1.0 M NaBr. (From ref. 5).

For polymer-surfactant systems, a segregative phase separation has been observed for many cases (ref. 5), including combinations of two nonionic cosolutes. An interesting illustration of the role of micellar size is given in Fig. 4, showing results for mixtures of dextran and ethoxylated alcohols (ref. 40). A segregative type of phase separation is observed, with the two-phase area being much larger for $C_{12}E_5$, which is known to form larger micelles. The temperature dependence is also striking since micelles of $C_{12}E_5$ but not of $C_{12}E_8$ are known to grow with increasing temperature. (Micellar growth also explains the change in the area of the two-phase region on addition of salt of the system shown in Fig. 4, since sodium dodecysulfate micelles are known to grow at addition of electrolyte.) For analogous systems with a more hydrophobic nonionic polymer, like a cellulose ether, an associative type of phase separation is observed; phase separation is favored by a temperature increase (ref. 41).

CONCLUSIONS

In the mixtures we consider, the concentrations are such that the surfactants occur in self-assemblies, in general micellar aggregates; it is observed that the critical micelle concentration of ionic surfactants is more or less strongly reduced in the presence of most polymers, polyelectrolytes of opposite charge giving particularly strong effects. Thus we are considering the mixing of solutions of two macromolecular species, which may be either a polymer molecule or an aggregate formed by a strongly cooperative self-association. The difference between a polymer solution and a micellar solution is, of course, the dynamical nature of the colloidal species in the latter case, with a rapid exchange of surfactant molecules between the monomeric and micellar states. The redistribution of surfactant molecules between micelles provides an important additional positive entropy contribution and explains why a segregative type of phase separation is not observed for surfactant mixtures and why surfactant mixtures are intrinsically different from polymer mixtures or polymer-surfactant mixtures. The latter two types of systems, on the other hand, appear to be closely analogous from a thermodynamic point of view and it appears fruitful to perform further comparative studies.

A complication for polymer-surfactant systems compared to the polymer-polymer mixtures is that the micelle size is variable with conditions. Moreover, the effect of the polymer on the aggregation number of the surfactant may be substantial, particularly if there is a strong attractive interaction. To analyze the phase behavior in detail it is, therefore, essential to investigate the surfactant aggregation number.

The phase behavior of these systems is complicated, but a qualitative rationalisation of the (pseudo) ternary phase diagrams, as well as their dependences on temperature (nonionic polymers) or added salt (polyelectrolytes) has nevertheless been shown to be possible within the Flory-Huggins theory (ref. 42-43).

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