

Intermolecular interactions and phase equilibria in colloidal systems

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Abstract - Colloidal systems often show a rich phase behaviour and the macroscopic properties of a particular system are strongly dependent on the phase characteristics. The study of phase equilibria is thus fundamental for understanding the basic features of colloidal systems. Another classical problem in colloidal science concerns the forces between particles, surfaces or aggregates, which are the result of complex interplay between many molecular degrees of freedom. Even though both the phase equilibrium and force problems have been extensively studied less attention has been given to the question how the forces between aggregates influence the phase behaviour. By way of examples it will be demonstrated how one from measured or calculated force-distance curves can deduce the phase behaviour. Conversely it will also be demonstrated how one can use observed phase behaviour to draw conclusions about surface forces. In addition the phase behaviour also can reveal an interesting interplay between long range and short range forces. By formulating a quantitative model that takes into account both the long range and short range interactions it is possible to obtain a rather detailed understanding of the phase behaviour of a particular system. In the presentation these general aspects will be discussed in relation to the molecular characteristics and phase behaviour of four types of systems.

INTRODUCTION

One of the classical challenges of the physical chemistry of liquids is to understand the relation between the microscopic molecular interactions and the macroscopic thermodynamic properties. In colloid science a thermodynamic property of high relevance is the phase equilibria since one often finds a much richer phase behaviour than in simpler liquids. Particularly for self-associating molecules, like surfactants in water, the phase behaviour is rich and it is essential in any study of such systems to establish the phase behaviour. This has led to an accumulation of a large amount of experimental data on phase behaviour. It is only during the recent years serious extensive attempts have been made to interpret these experimental findings in terms of microscopic models. There is a twofold purpose of establishing such relations between molecular interactions and phase behaviour. The observed thermodynamic equilibrium data provides information on the situation on the molecular level that can be very difficult to obtain by other means. On the other hand a good understanding of the molecular features that are controlling the equilibrium between different phases makes it possible to design systems with desirable phase properties.

Below we will discuss four different examples how one can understand the relation between phase behaviour and molecular interactions. These four cases are chosen to illustrate different approaches to the problem and it will become evident that depending on the particular chemical nature of the problem the modelling involves rather different conceptual frameworks. The four problems chosen are

- i) the effect of cholesterol on phospholipid phase behaviour
- ii) phase equilibria in ionic surfactant systems
- iii) the nature of the L_3 phase
- iv) incompatibility in aqueous two polymer systems.

CHOLESTEROL IN PHOSPHATIDYL CHOLINE SYSTEMS

Cholesterol is an abundant component in some biological membrane systems, such as the human plasma membrane, while it is absent in others. The physiological role of cholesterol is still debated and one clue to clarify this problem should lie in the change in membrane lipid phase behaviour induced by cholesterol. Consequently a large number of, more or less systematic, investigations have been devoted to establish the phase behaviour of model systems containing cholesterol. Particularly well studied is the system dipalmitoyl phosphatidyl choline (DPPC)-cholesterol in excess water. The most careful and complete study is due to Vist and Davis (ref. 1 and 2), which is in agreement with a number of previous investigations. The resulting phase diagram up to a mole fraction cholesterol of 0.3 is shown in Fig. 1.

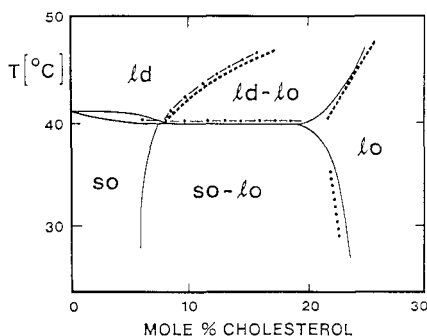


Fig. 1.

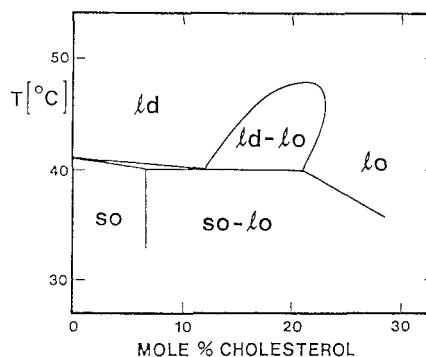


Fig. 2.

Fig. 1. Partial phase diagram of DPPC-cholesterol in excess water. Both the *lo* (liquid ordered) and *ld* (liquid disordered) are lamellar liquid crystalline phases while the *so* (solid ordered) is a gel phase. (From ref. 3.)

Fig. 2. Calculated phase diagram using a regular solution theory and a two state model for DPPC.

This phase diagram shows three unusual features. The most striking is the coexistence of two lamellar liquid crystalline phases. What molecular mechanism is driving this phase separation, where in both phases DPPC is the most abundant species? The second unusual feature is that at low cholesterol contents there is a very narrow two phase region at nearly constant temperature, showing that cholesterol is as soluble in the solid (gel) phase as it is in the liquid crystalline phase. Normally a liquid is a vastly better solvent than the corresponding solid and this rule still applies to (quasi)-two-dimensional systems albeit less strongly. What molecular mechanism could possibly account for the observation that cholesterol is as happy in the solid, where it is bound to perturb the crystalline order, as it is in the liquid crystalline phase? This question becomes even more demanding when one includes the third noticeable feature that at higher cholesterol contents the lamellar liquid crystalline phase is stable to very low temperatures.

Taking advantage of the careful NMR studies of acyl chain order (ref. 1 and 2 and references therein) it turned out to be possible to account for the observed phase behaviour within a simple model (ref. 3) having the following ingredients:

- i) The DPPC molecule exists in two classes of conformational states. This is modelled by a two state model, ordered chains (*o*) with low entropy and energy and disordered state (*d*) with high entropy and energy. Such models have been used to model phase transitions in DPPC (e.g. ref. 4).
- ii) A DPPC molecule prefers a neighbour in the same state relative to one in the other state. This is from a molecular point of view a very reasonable assumption.
- iii) Cholesterol interacts preferentially with a DPPC molecule in the *o* state. That this is the case emerges clearly from the NMR studies (ref. 1 and 2) which show that acyl chain order increases with increasing cholesterol content.
- iv) In the solid state DPPC is exclusively in the ordered state *o* and there exists in addition a long-range chain order, which is disturbed by the insertion of a cholesterol molecule.

The observation that cholesterol is equally soluble in the *so* and the *ld* phases emerges as a cancellation of two effects. Locally a cholesterol molecule prefers an *o* chain rather than a *d* chain, while there is a free energy cost in the distortion of the crystalline phase in the *so* phase. Using conventional regular solution theory with the addition of the two state model for the DPPC one can calculate a phase diagram shown in Fig. 2.

The phase diagram in Fig. 2 shows all three of the unusual features of the experimental diagram shown in Fig. 1. The parameters used to obtain the calculated diagram all have quite reasonable magnitudes (see ref. 3) and although a fitting procedure is involved it turned out to be difficult to find a parameter set that reproduces only two and not the third of the unusual features, showing that the three phenomena are interconnected.

IONIC SURFACTANT SYSTEMS

For ionic surfactants electrostatic, double layer, interactions play a dominant role in determining the concentration dependence of phase stability. The formation of a micelle or a liquid crystalline phase leads to high local concentration of charges and aggregate formation involves a cost in electrostatic free energy.

The electrostatic contribution to the free energy can be conveniently described within the framework of the mean field Poisson-Boltzmann equation. Although many approximations are involved in arriving at this equation it provides a surprisingly accurate description (ref. 5). As an example of

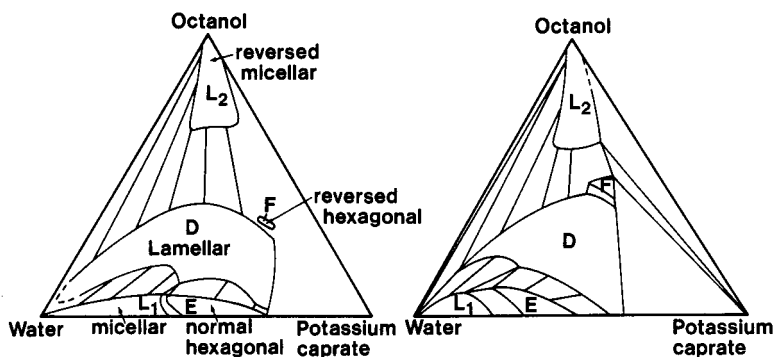


Fig. 3. Experimental (left) and theoretical (right) phase diagrams for the system water-potassium caprate-octanol (adapted from ref. 7).

what can be achieved Fig. 3 shows the experimental phase diagram of the system water-potassium caprate-octanol (ref. 6) and the corresponding calculated diagram taken from ref. 7.

Apart from a Poisson-Boltzmann description of the electrostatics the model calculation contains contributions from hydrophobic interactions including a term for the interfacial energy polar-apolar medium and a contribution from the entropy of chain mixing in phases of the reversed type.

The behaviour in the water-rich corner is dominated by the electrostatic effects. For the binary surfactant-water system the charge density on the aggregates is very high favouring a micellar phase at high water contents. Somewhat counterintuitively the importance of the electrostatic effects decrease with increasing concentration and this leads to the formation of liquid crystalline phases at higher surfactant concentration. The addition of alcohol to the system has two effects. There is a reduction of the charge density in the aggregates making the formation of hexagonal and particularly lamellar phases more favourable. There is also a, from a quantitative point of view, important reduction in the interfacial free energy. The lamellar phase can incorporate large amounts of water due to the repulsive double layer force acting between two charged surfaces. Thus when the alcohol content in the lamellae is optimal there can be an extensive swelling of the lamellar phase.

An interesting effect appears when one substitutes the monovalent counterion for a divalent one. Figure 4 shows three systems with the same alcohol and surfactant anion but with varying counterion. With sodium as counterion the behaviour is quite analogous to the one shown in Fig. 3 while with divalent counterions the situation is still much the same but there is no extensive swelling of the lamellar phase (D).

This qualitative behaviour has also been found in a number of other ionic surfactant systems (ref. 8 and 9).

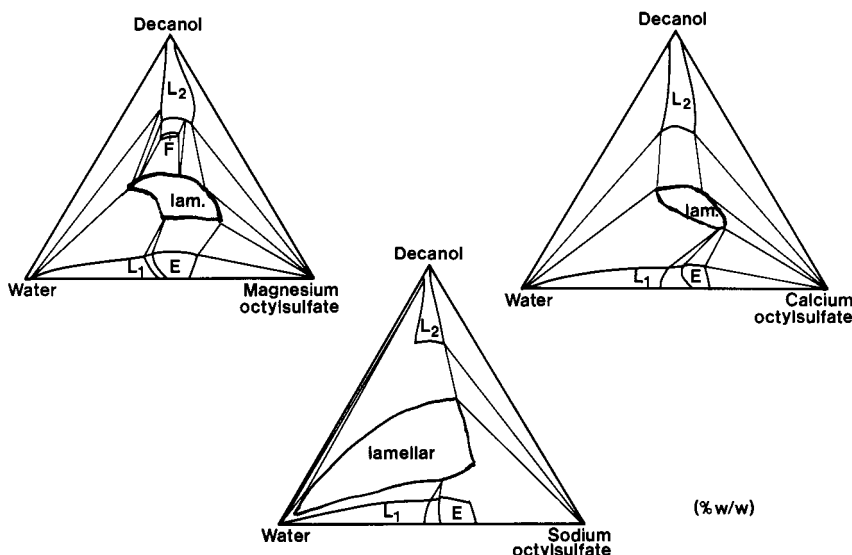


Fig. 4. Three experimental phase diagrams for the systems water-decanol-cation octylsulfate with Mg, Ca and Na as counterions. (Adapted from ref. 5.)

A description based on the Poisson-Boltzmann equation cannot explain these results (ref. 9). We have concluded that they provide a clear demonstration of the prediction, that similarly charged surfaces can attract each other if they are sufficiently highly charged and/or have high counterion valency (ref. 10-14). This effect is qualitatively different from the normal textbook description of double layer interactions and when observed previously it has usually been attributed to specific binding or special bridging effects. In fact it is a purely electrostatic effect appearing beyond the mean field description of the Poisson-Boltzmann equation. In this case phase equilibrium studies have been the most successful in establishing the presence of this attractive electrostatic component of the force between two charged surfaces.

THE NATURE OF THE L_3 PHASE

In a number of chemically rather different surfactant systems one observes that a narrow isotropic phase appears between a lamellar phase and a dilute isotropic solution. This phase contains large aggregates and is usually called the L_3 phase (ref. 15) or the anomalous phase (ref. 16). Examples of systems having the L_3 phase is shown in Figs 5 and 6.

A very characteristic feature of the L_3 phase is the narrow character of the one-phase region similar to those found for stoichiometric intermediate compounds. This indicates that there is an inherent constraint of a chemical nature reducing the effective degrees of freedom from two, as given by the Gibbs' phase rule, to essentially one. From a systematic study of the conditions where the L_3 phase is formed one can first conclude that the occurrence of the phase is due to some general physical effect since the phase occurs in practically all types of surfactant systems. In addition its occurrence is correlated with the occurrence of lamellar liquid crystalline phases. A closer examination (see ref. 18) also shows that the phase occurs when a surfactant monolayer has a small spontaneous curvature towards the abundant solvent. Using the theoretical framework of differential geometry one can show that it is possible to form aggregates, extending in three dimensions, that have a surfactant bilayer as the local structure such that the polar-apolar interface curves towards the solvent. The surface formed by the midplane of the bilayer should be close to a minimal surface (ref. 18) and it is, by virtue of the Gauss Bonnet theorem of differential geometry, highly connected. Similar ordered structures have been found for cubic liquid crystals.

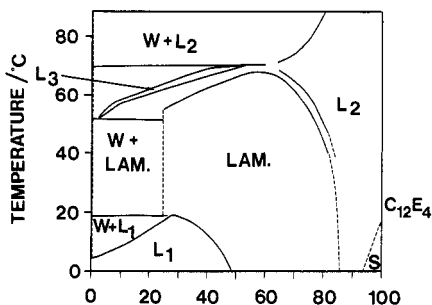


Fig. 5. Phase diagram of the system $\text{H}_2\text{O}-\text{C}_{12}\text{H}_{25}(\text{OC}_2\text{H}_4)_4\text{OH}$ (adapted from ref. 15).

TABLE 1. Temperature T_0 at which the spontaneous curvature of a surfactant monolayer is zero for water $\text{C}_n\text{H}_{2n+1}(\text{OC}_2\text{H}_5)_m\text{OH}$.

Surfactant	T_0
C_{16}E_4	35.0
C_{12}E_4	53.5
C_{10}E_4	45.3
C_{12}E_5	64.5

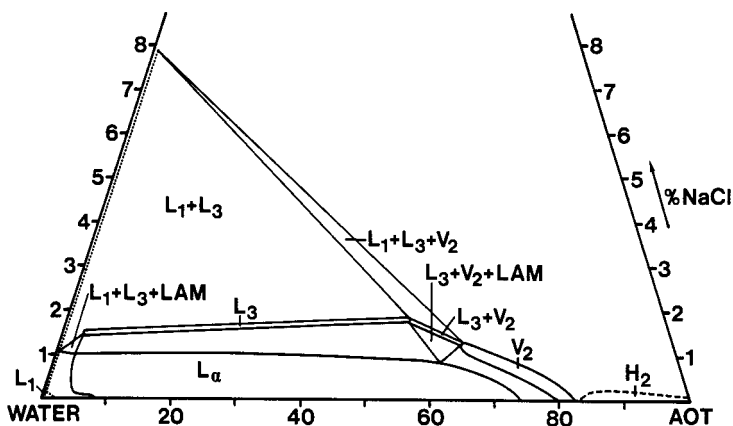


Fig. 6. Phase diagram of the system water-NaCl-AOT (adapted from ref. 17).

The assumption that the aggregates in the L_3 phase has an average mean curvature equal to spontaneous curvature, all counted at the polar-apolar interface, provides an extra constraint that can only be satisfied at a given volume fraction of bilayer. This provides a direct explanation of the narrow character of the L_3 phase.

Having established a relation between volume fraction bilayer and monolayer spontaneous curvature, it is possible to use the observed phase behaviour to calculate the spontaneous curvature. As an example of such a calculation Table 1 shows the temperature at which the lamellar phase of nonionic surfactants is optimally stable.

POLYMER INCOMPATIBILITY IN AQUEOUS SOLUTION

A range of pairs of water soluble polymers show incompatibility at moderate concentrations in water, *i.e.* they phase separate into two isotropic solutions of approximately the total polymer concentration but with one polymer enriched in each phase. These systems have found an extensive use in a biochemical separation technique (ref. 19) termed aqueous two phase partitioning. Although these systems have been extensively studied from the point of view of optimizing the separation performance, few studies have been devoted to the more fundamental physico-chemical reason for the phase separation. The basic cause of the polymer demixing is the small entropy involved in mixing entire polymer molecules. The major entropy contribution leading to polymer solubility in a solvent is due to the entropy of the internal degrees of freedom. This entropy is, to first order, only dependent on the total polymer concentration and has then the same magnitude in a one as in a two polymer solution. It is thus sufficient with only a rather weak polymer 1 - polymer 2 effectively repulsive interaction to cause a phase separation. This effect can be semiquantitatively modelled within the Flory-Huggins theory of polymer solutions. This is illustrated in Fig. 7 for the experimentally most studied system water-polyethyleneoxide-dextrane (see ref. 20).

The Flory-Huggins theory is somewhat problematic for aqueous polymer systems since the real system has more relevant degrees of freedom than assumed in the basic theory. Thus the interaction parameters in the theory represent thermal average over several degrees of freedom and they are intrinsically temperature dependent. This effect is particularly apparent for polyethyleneoxide which phase separates in water at higher temperatures. This decreasing affinity for water at higher temperature has also consequences for the ternary system water-polyethyleneoxide-dextrane at higher temperatures. Fig. 8 shows the phase diagram at 80 °C.

A comparison between Figs 7 and 8 reveals that the major effect of the temperature rise is that the tielines tilt differently. At the higher temperature the polyethylene-rich phase has a relatively lower polymer concentration, reflecting the decreased affinity for water of the polyethylene oxide. The calculated lines in Fig. 8 is obtained from an extended Flory-Huggins theory assuming a two state conformational model for polyethyleneoxide due to Karlström (ref. 21).

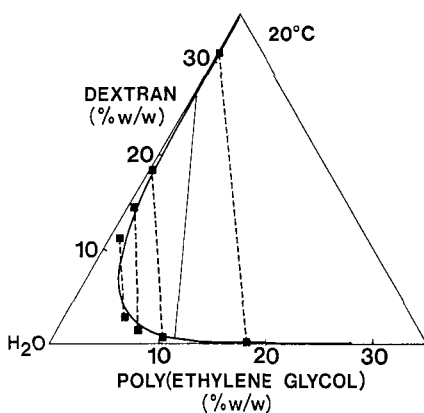


Fig. 7.

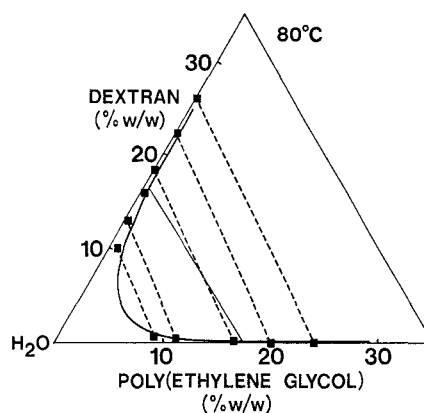


Fig. 8.

Fig. 7. Experimental and calculated phase diagram for the system water-polyethyleneoxide-dextrane at 20 °C (adapted from ref. 17). experimental points, solid line calculated curves, with some tielines shown.

Fig. 8. The phase diagram water-polyethyleneoxide-dextrane at 80 °C; experimental points, solid line theory. (From ref. 21.)

CONCLUSION

Above we have shown through four different examples how phase equilibrium studies can be used to establish information on molecular interactions. For the cholesterol-phosphatidylcholine system it was shown how the preference of cholesterol for a straight acyl chain conformation could lead to an anomalously high cholesterol solubility in the phosphatidylcholine gel phase and also through basically the same effect to a lamellar-lamellar phase coexistence. For ionic surfactant systems it was shown how phase studies could be used to establish the conditions under which the Poisson-Boltzmann approximation adequately described the interaction between charged surfaces. From the observation of an L_3 phase one can obtain qualitative and quantitative information on the spontaneous curvature of surfactant monolayer. Finally it was pointed out that the temperature dependence of the water-polyethyleneoxide-dextrane phase equilibria can be used to obtain information on both the dextrane-polyethyleneoxide and the polyethyleneoxide-water interaction by using the theoretical framework of the Flory-Huggins theory.

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