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ORIGINAL CONTRIBUTION

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Hydrogels in aqueous phases of polyvinylalcohol (PVA), surfactants and clay minerals

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Abstract Aqueous solutions of synthetic clay minerals have been studied in the presence of surfactants and water-soluble polyvinylalcohol (PVA). The PVAs (PVA 1, PVA 2) had a molecular weight of about 10^5 Dalton and a degree of hydrolysis of 82%. The PVA-samples were surface active and lowered the surface tension to 43 mN/m. As a consequence of their amphiphilic nature the PVA molecules bind strongly to clay mineral particles. On saturation the clay mineral particles adsorb the fivefold weight of PVA of their own weight. It is concluded that the thickness of the adsorbed layers on both sides of the clay mineral is in the range of the hydrodynamic diameter of the PVA-coils in the bulk phase.

When the clay mineral particles are not saturated with PVA, they act as cross-linking agents for the PVA. The whole systems are physically cross-linked and assume gel-like properties. Rheological measurements show that samples behave like soft matter with a yield stress value. All of them have a frequency independent storage modulus which is an order of magnitude larger than the loss modulus. The hydrogels become stronger as PVA concentration increases.

Small amounts of cationic surfactants bind on the clay mineral. The interface of the clay mineral becomes more hydrophobic and the binding of the PVA on the clay mineral is strengthened. With rising concentration of the surfactant the surfactant molecules bind on PVA and the PVA becomes hydrophilic. As a consequence the PVA can no longer bind on the clay mineral and the gels transform to viscous and turbid solutions. Small amounts of cationic surfactants therefore stiffen the hydrogels while larger amounts cause phase separation and a solution with low viscosity. Anionic surfactants like SDS do not bind on the clay mineral, but strongly on the PVA. With increasing SDS concentration, the hydrogels become stiffer at first but thereafter they break and transform to viscous fluids.

In PVA-solutions without the clay minerals both cationic and anionic surfactants bind to the PVAs in the aqueous solution. With increasing concentration of surfactant, the viscosities of the solutions pass over a maximum. In this respect the PVAs behave like hydrophobically modified water soluble polymers. The surfactants bind to the hydrophobic microdomain and thereby crosslink the polymer molecules. On saturation the polyvinyl alcohol with anionic surfactant become hydrophilic and the network character disappears to a certain extent.

Keywords Hydrogels · Clay minerals · Polyvinyl alcohol · Polymer surfactant interaction

Introduction

Aqueous formulations for agrochemicals, detergency, cosmetics and pharmaceutical applications can contain water-soluble polymers, surfactants and clay minerals [1]. Water-soluble polymers are added for various reasons. They can function as dispersive agents, as thickeners or, under special applications, can prevent the blooming of dyed textiles. Water-soluble polymers are amphiphilic compounds and surface active. Therefore they adsorb on solid surfaces like clay mineral [2, 3]. Surfactants can also bind on clay mineral [4]. They compete with the polymers for the adsorption area on the clay mineral. However, the surfactants can also bind to the polymers. This causes a change in the conformation of the polymer [5]. All the various interactions have an influence on the macroscopic properties of the systems and the situation in systems with all the mentioned components can be very complex. Investigations have usually been made on all possible binary systems like aqueous clay mineral dispersions, surfactant or polymer solutions.

Some measurements have also been done on ternary systems like polymers and surfactants in water [6, 7]. For some polymer/surfactant combinations both the binding constants of surfactants to polymers and the amount of surfactants that can bind on the polymer under saturation [8] are well-known. These measurements also were carried out for ternary systems of clay mineral and surfactant in water [9], respectively for ternary systems of clay mineral and polymers in water [3, 10, 11].

In the present study we shall present some experimental results on the quaternary systems clay mineral, surfactant, polyvinyl alcohol and water. First we present some information on the components, then we take a look at the binary and ternary systems and finally discuss some systems in which all the components are present.

Experimental

Materials The polyvinyl alcohols, PVA 1 and PVA 2, were provided by Wacker Chemie. Two synthetic clay minerals—SKS-20 and SKS-21(Saponite)—were provided by Clariant GmbH, sodium dodecyl sulfate (SDS) from Serva Feinbiochemica GmbH & Co and tetradecyltrimethylammonium bromide (TTAB) from Aldrich Chemie. All compounds mentioned were used without special treatment.

Preparation of solutions and gels For the two-component system polyvinyl alcohol and water, a certain amount of polyvinyl alcohol was added to deionised water under stirring. The mixture was stirred for 36 h at 70 °C. The turbid solution became transparent as its concentration increased. However, a small amount of some white precipitate remained in the solution. That was removed by filtration.

For a three-component system—polyvinyl alcohol, saponite and water—the polyvinyl alcohol was dissolved at first in water at 70 °C; then saponite was added into the solution; finally the mixture was stirred for 24 h at 70 °C. In order to investigate the phase diagram of 2.0 wt% SDS + 2.0 wt% SKS-20 + 2.0 wt% PVA 2, these solutions or gels were prepared respectively. Then the solutions were mixed according to different ratios.

Measurement and characterisation Surface tension measurements were made on a Lauda tensiometer TE1C/3 by the ring method. Viscosity measurements were carried out on Haake RS600. The measuring device consists of a cylinder-double gap set-up. The oscillation test was done by a cone-plate system on Haake RS 300. The deformation was fixed to 5%. Dynamic light scattering (DLS) was performed on an ALV DLS/SLS-SP 5022F compact goniometer system with an ALV 5000/E correlator and a He-Ne laser with a wavelength $\lambda = 632.8$ nm. The samples were filtered using Millipore Teflon filters with a pore size of 0.45 mm before the light scattering measurements were made. Static light scattering was examined on a KMX-6 low angle laser light scattering photometer.

Results

The binary polymer water systems

The static light scattering (SLS) data in Fig. 1 show the typical behaviour of aqueous polymer solutions. In the concentration range between 0 and 0.015 g/ml, the interaction between dissolved coils is repulsive. Therefore there exists no aggregation. Dynamic light scattering (DLS) data show a single correlation function at concentrations below 1% and an indication of a longer correlation function at around 1% and higher concentrations (Fig. 1b). The slow correlation function could be taken as evidence for aggregation of PVA. Since there is no evidence for aggregation in the static light scattering results, it is more likely that the slow correlation function comes from the interaction of the overlapping chains. Such slow modes are often observed in polymer solutions. Another possibility is different sensitivity of DLS and SLS. The aggregation of PVA is easier to probe by DLS.

The surface tension measurements in Fig. 2 show that the polymers are surface active and the surface tension decreases linearly with log c. The slope of PVA 1 is steeper than that of PVA 2. This means that the required area of the polymer PVA 1 at the surface is smaller than that of PVA 2. This is consistent with the fact that the polymer PVA 1 shows a lower surface tension than polymer PVA 2. As a consequence of the larger hydrophobicity, the coils seem to be more compact. For larger concentrations the σ-log c curves show a break and become independent of the concentration.

For surface active compounds, such a break would be an indication of a critical micelle concentration and a sign that the polymers form aggregates and micelles. In

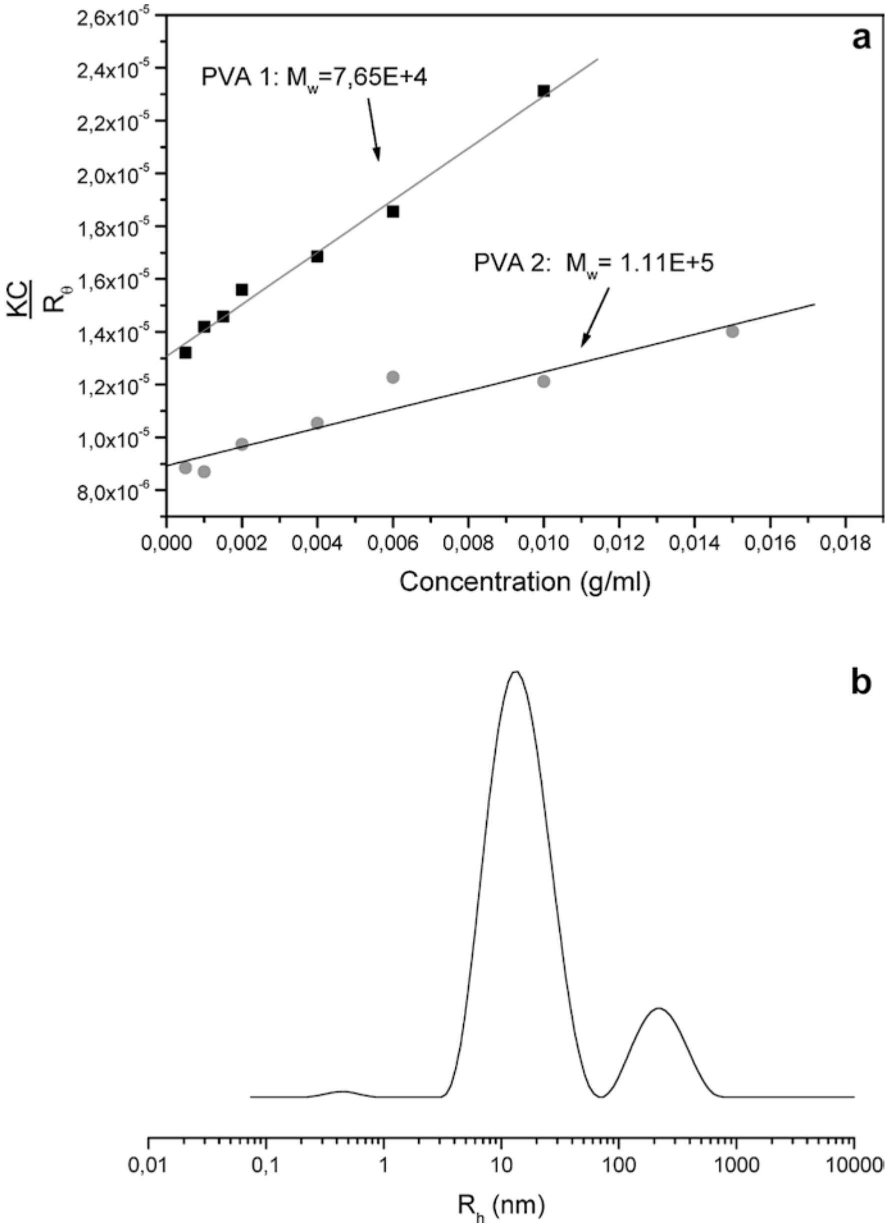

Fig. 1 **a** Static light scattering results of aqueous polyvinyl alcohol solutions. **b** Dynamic light scattering measurement of 0.5 wt% PVA 2 solution at 90° angle

the present situation this does not seem to be the case because the light scattering does not show aggregates. The reason for the break of the surface tension does not lie in the bulk phase but in the adsorption layer at the surface. It seems conceivable that the polymer concentration saturates at the interface and no more molecules can be squeezed into the monolayer. The area "a" that was determined for the polymers at the surface is given in Table 1 together with the molecular weight and the hydrodynamic radius for the polymer coils. The "a" values are much less than the cross-section of the coils that are obtained from the light scattering data. It is, therefore, likely that the coils adsorbed at the surface form a very compact structure in comparison to those in bulk solution.

As revealed by Fig. 3, there are obviously two different states for both PVA chains. Below 1 wt%, PVA forms Gauss coils. There is no interaction between the PVA molecules. This situation changes slowly as the concentration increases above 1 wt%. The interaction becomes strong because of overlapping PVA chains. If the PVA coils below 1 wt% are presumed to be hard particles and obey the Einstein equation: $\eta = \eta_0(1 + 2.5\phi)$ (η_0: viscosity of solvent, ϕ: volume fraction of solute), it is possible to evaluate an effective volume fraction for the polymer coils and compare these values with the

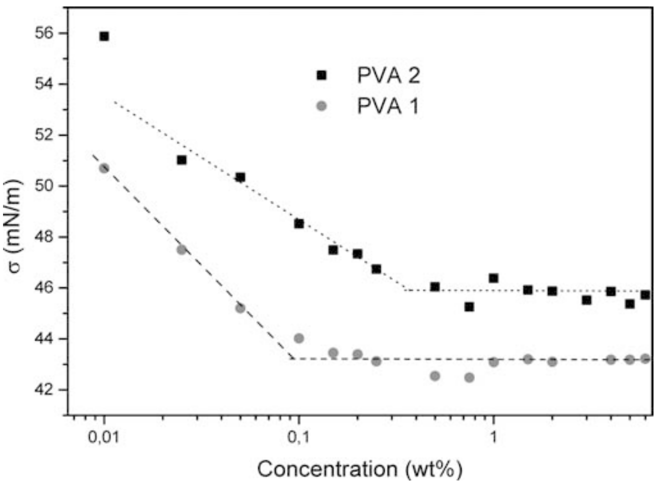

Fig. 2 Surface tension against concentration for aqueous polyvinyl alcohol solutions

Table 1 PVA molecular parameter derived from measurement of surface tension, dynamic light scattering and viscosity

	M_w (g/mol)	a (nm^2)	R_h (nm)		φ_{eff}	φ
			Low peak	High peak		
PVA 1	76,500	1.50	7.3	91.0	0.15	0.069
PVA 2	111,000	2.27	14.2	185.7	0.24	0.33

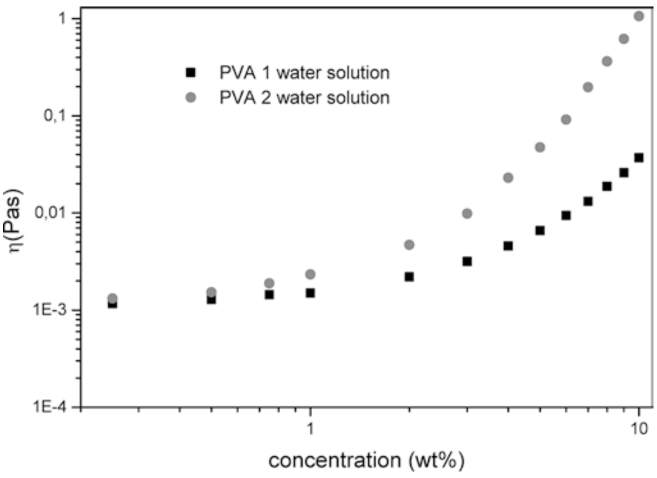

Fig. 3 Viscosity against concentration for aqueous polyvinyl alcohol solutions

polymer volume in the solution. These values are also given in Table 1. The data show that the volume of the polymer coils is similar to the densely packed polymer. In diluted solutions the swollen coils behave as hard particles.

The binary system water-clay mineral and the ternary system water/clay mineral/surfactant

Information on dispersions of the clay mineral in water have been given by several groups [12, 13]. The clay mineral has an ion exchange capacity of 88 mg/100 g dry clay mineral. In aqueous dispersion, the particles are completely delaminated. Cationic, zwitterionic and nonionic surfactants bind on the clay mineral [9]. With increasing concentration of the surfactant the surface of the clay mineral becomes hydrophobic and the clay mineral flocculates. On further increase of the surfactant concentration an excess surfactant bind and the clay mineral is redispersed.

The system water/clay mineral/polymer

In order to determine the adsorption isotherms of the polymers on the clay mineral, surface tension measurements were carried out. In Fig. 4 we show the surface tension of 1% clay mineral dispersions with increasing concentration of the polymers. For comparison the results for the polymer solutions without clay mineral are given.

The data show that the polymers bind on clay mineral. This is not unusual and has been well-known for a long time [11]. In the presence of the clay mineral the surface tension reaches the low value for saturation at a much higher polymer concentration then without the clay mineral. From these values it is possible to calculate the total amount of adsorbed polymer per gram clay mineral. The results indicate that the clay mineral particle can bind four times their weight of the polymers. This gives us an indication of the microstructure of the adsorbed polymers. We could imagine that the coils

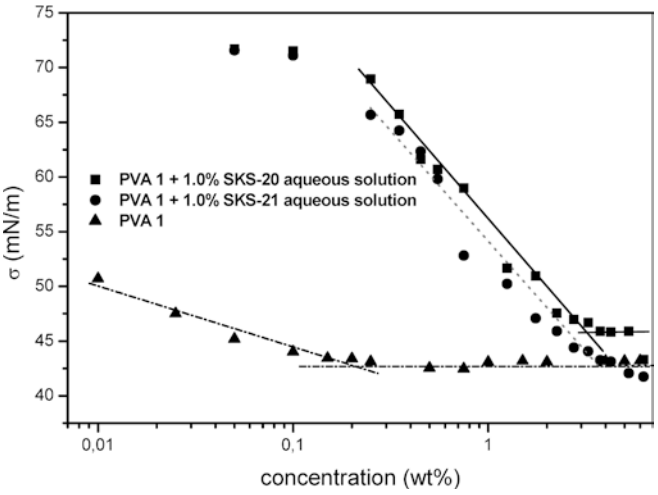

Fig. 4 Surface tension against polymer concentration for clay mineral dispersion in PVA 1 solutions

unwind and adsorb as a monolayer at the surface of the clay mineral. With such a model only 0.12 g of polymer could bind to 1 g clay mineral.

If we assume that the whole coils adsorb on the clay mineral and form a densely packed film, the adsorption values are close to the experimental values. It is therefore likely that the coils adsorb on clay mineral without changing their conformation very much. For high polymer concentration the surface tension values show a break before they reach the same low values of the pure polymer solutions without clay mineral. This effect is probably due to the experimental difficulty in measuring the exact surface tension values. For high clay mineral and surfactant concentration the solutions become gel-like and have a yield stress. It is obvious that an additional force must be exerted to deform the gel when the surface tension measurements are made.

Hydrogels of clay mineral, polymer and water

If dispersions with 0.5–1.5% of clay mineral are mixed with increasing concentration of the polymers and the solutions are left standing for a few days, the systems separate in two liquid phases with a sharp phase boundary in between the two phases (Fig. 5). The lower phase is somewhat turbid and contains most of the clay mineral particles and polymer while the upper phase is clear. The volume fraction of the lower phase increases with increasing polymer concentration and finally fills up the whole volume. It is a viscoelastic phase with gel-like properties (Fig. 6). The phase does not flow when the sample is tilted. It also shows a strong birefringence under deformation. It is obvious that the viscoelastic phase has a yield stress. Figure 7 shows that the phase behaves like a Bingham fluid. It starts to flow when the applied shear stress is larger than the yield stress. The oscillating rheogram in Fig. 8 reveals the typical behaviour of soft gels. The storage modulus is frequency independent and about an order of magnitude larger than the loss modulus. The storage modulus depends somewhat on the polymer/clay mineral ratio. Generally higher polymer concentration leads to a higher storage modulus. Obviously, the viscoelastic properties of the system are caused by formation of a physical network.

The ternary system: water/polymer/surfactant

In the past, many aqueous solutions in the presence of polymers and surfactants have been studied [5, 6, 14]. In such regimes one has to distinguish between systems in which the surfactant bind to the polymer and systems where the surfactant does not bind to the polymer. Both situations can lead to phase separation [15]. In the case of no binding, the phase separation can be caused by depletion flocculation [16]. The interaction between the micellar and the polymer coils is repulsive. The consequence is that one phase contains mainly the polymer and the other phase the surfactant. In the situation

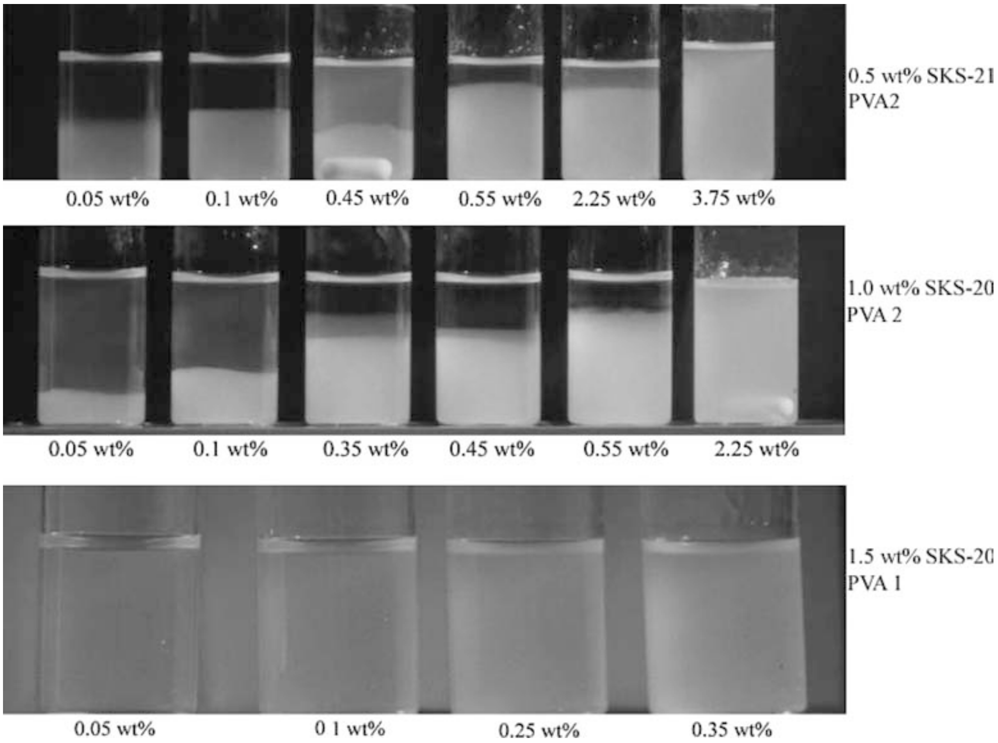

Fig. 5 Phase transition of polyvinyl alcohol + clay mineral system

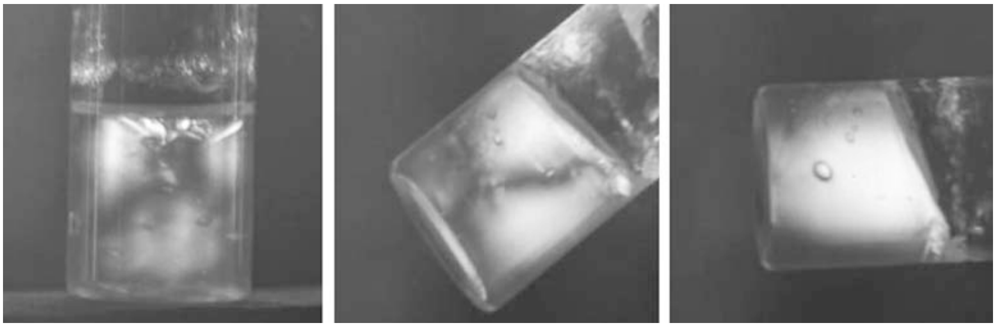

Fig. 6 Birefringence of gel of 5.25 wt% PVA + 1.5 wt% SKS-20

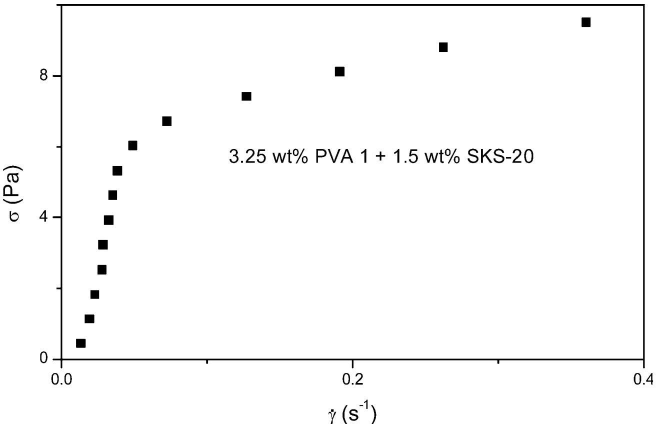

Fig. 7 A typical yield stress measurement for gels of polyvinyl alcohol + clay mineral

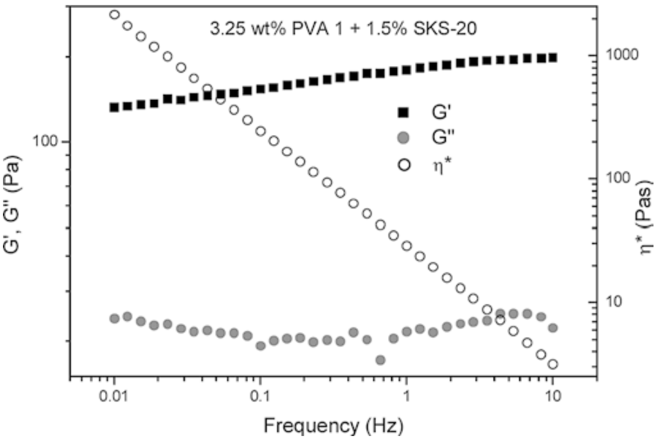

Fig. 8 A typical rheogram for gels of polyvinyl alcohol + clay mineral

where the interaction is attractive, one phase contains polymer surfactant aggregates while the other phase consists mainly of water [17]. In between these two extreme situations there can be situations where the surfactant bind to the amphiphilic polymer, but the binding does not lead to phase separation.

Systems of this type which have been studied in detail are polyethylenoxide in the presence of sodium dodecylsulfate (SDS) and polyvinylpyrrolidons with SDS [7, 18, 19]. Of additional special interest in these systems is the concentration from which the surfactant begins to bind at the polymer solution [20] and the quantity of surfactant which is absorbed on the polymer. The binding between the surfactant and the polymer could be highly co-operative [21]. It is also interesting to know whether the conformation remains the same in the presence of the bound surfactant or not. These questions can be solved by the use of different techniques like electric birefringence measurements, EMF-measurements with surfactant specific electrodes and sometimes simply by surfaces tension measurements.

Some measurements have been published for PVA and various surfactants. The cationic surfactant CTAB starts to bind to PVA at a concentration of about 0.1 CMC. These measurements have been carried out at low surfactant and polymer concentration where the macroscopic properties of the solution are not much affected by the polymer surfactant complexes.

The saturation concentration of the polymer with surfactant is most easily done with the help of surface tension measurements (Fig. 9). In the presence of the polymer a higher surfactant concentration is required to reach the surface tension value where the surfactants start to form micelles. A plot similar to Fig. 9 is shown in Fig. 10 for the binding of PVA to SDS. In Fig. 9, the adsorption of SDS on both of polymer is same, about 1.0 g/g polymer. In Fig. 10, Adsorption of SDS on PVA 1 is 0.58 g/g polymer and on PVA 2 is 0.29 g/g polymer. The reason for this difference lies in poor surface activity of the polymers. Polymer affects surface tension of the mixed solution far less than SDS, which is also proven by the difference of the saturation points in Figs. 9 and 10. In Fig. 10 the point is not as clear as in Fig. 9. So the use of the latter method is not so good to determine adsorption of SDS. At higher polymer concentration the binding of the surfactants influences the macroscopic properties of the solutions. This is clearly expressed in the viscosity of the solutions. With increasing SDS concentration the viscosity of the PVA solution is

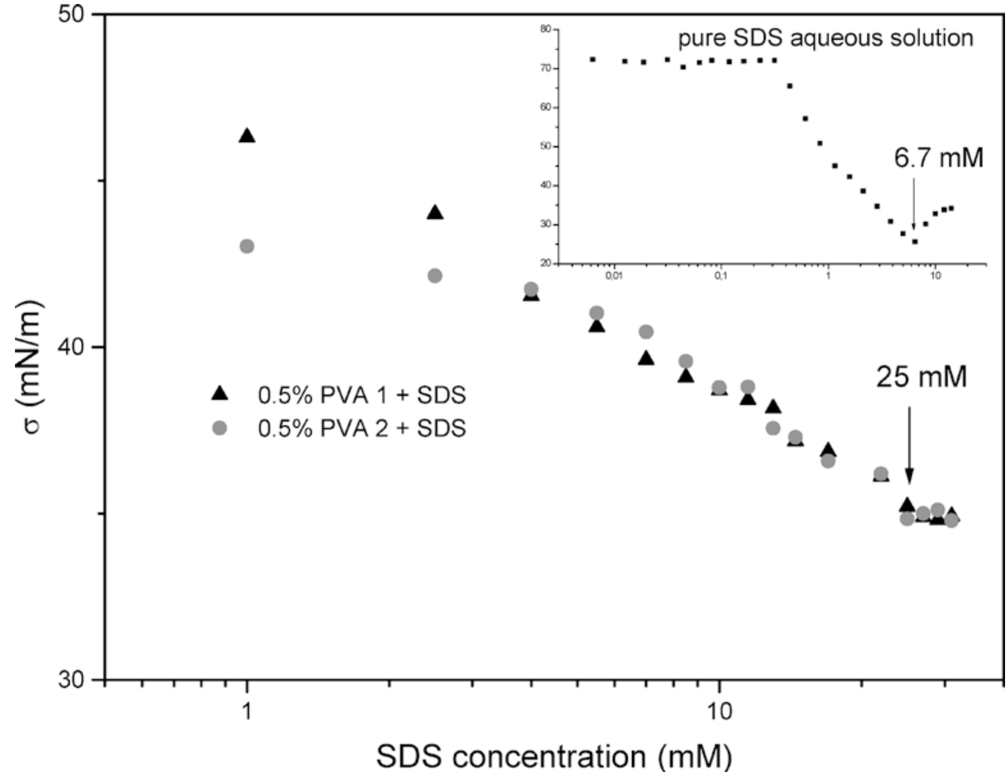

Fig. 9 Surface tension against concentration for aqueous polyvinyl alcohol + SDS solutions

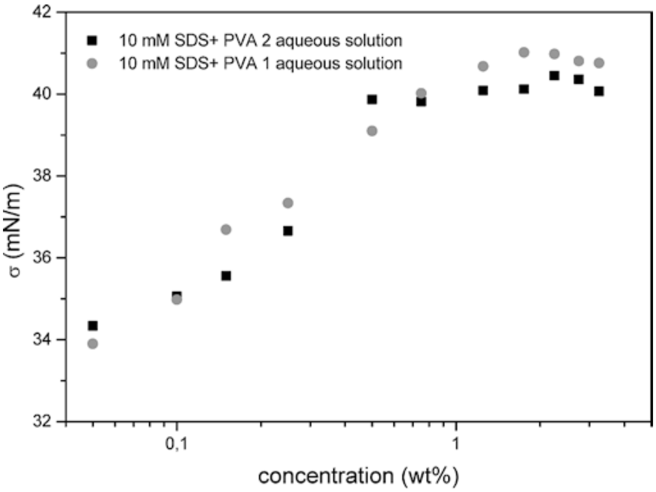

Fig. 10 Surface tension against polymer concentration for aqueous polyvinyl alcohol + SDS solutions

increasing, passes over a maximum and than drops sharply (Fig. 11). In this respect the PVA molecules behave in the same way as hydrophobically modified polymers. The surfactants bind to the hydrophobic microdomain and crosslink the polymers. As a consequence the whole system is transformed into a dynamic network. When the hydrophobic groups are finally saturated with surfactants, the crosslinks are destroyed and the viscosity decreases to the viscosity of the polymers. For higher SDS concentration micelles are formed and the ionic strength of the system rises. As a consequence the dimension of the polymer/surfactants complex shrinks.

The quaternary system: water/clay mineral/polymer/surfactant

Since the projection of such a three-dimensional object on a plane and the evaluation of a point in this object is a difficult processes, we have chosen a pseudo ternary system for the representation of the phases in the normal triangular representation. As the corners of our triangle we choose a 2% solution of each component in water. This gives us the possibility to map out single and multiphase regions. Such a triangle is shown in Fig. 12. In Fig. 13 we show the complex viscosity and the modulus at a frequency of 1 Hz when we pass from the clay mineral/polymer base line to the surfactant corner. With increasing concentration of anionic surfactant the viscosity and the modulus increase reach the maximum and finally both parameters break down, and a low viscous system is reached. A similar phenomenon is also observed with the cationic surfactant TTAB. The above behaviour is probably a result of the following situation. Small amounts of the cationic surfactants bind strongly to the clay. The surface of the clay mineral becomes more hydrophobic and the

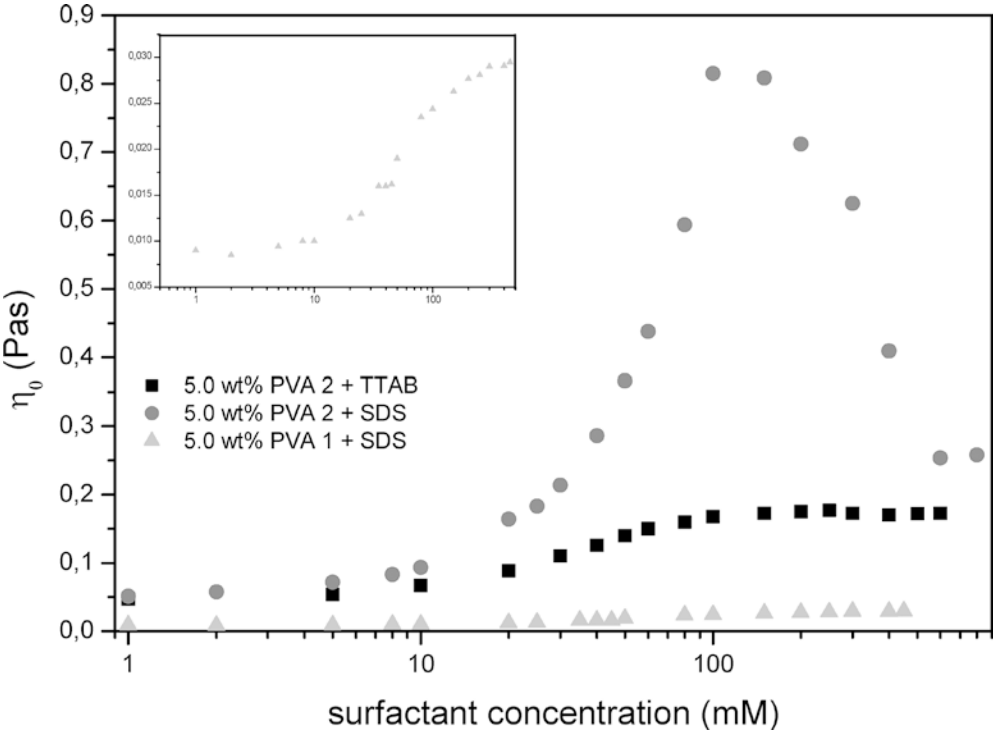

Fig. 11 Zero shear viscosity of PVA + SDS/TTAB as a function of SDS/TTAB concentration

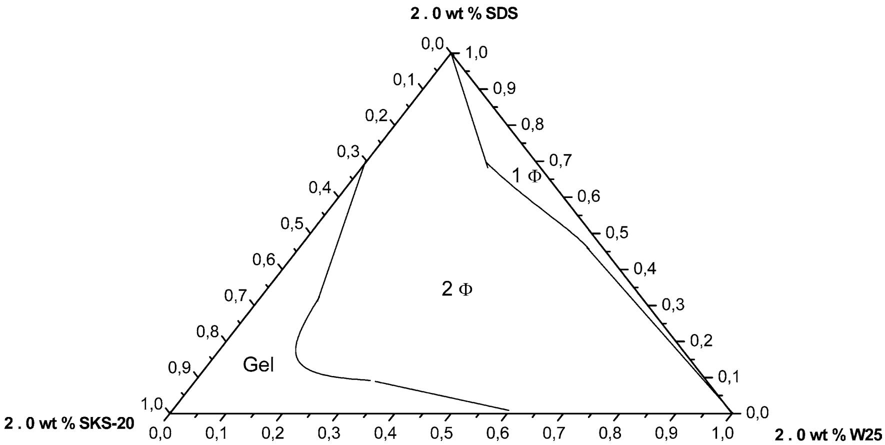

Fig. 12 Phase diagram of the quaternary system: water/clay mineral/polymer/surfactant

polymer can now bind better on the modified surface of the clay mineral. That results in an increase of the shear modulus. At higher concentration the surfactant molecules bind on the PVA. The PVA becomes more hydrophilic and the polymer can no longer bind to the clay mineral. The network breaks down. So the increase of surfactant concentration dilutes the crosslink number between PVA and clay minerals and the gels will be destroyed. With rising concentration, the surfactant activity increases. More surfactant can bind to the clay mineral and because of the charge compensation the clay mineral will flocculate. With the anionic surfactants, the flocculation does not occur. The depletion effects induce phase separation between the clay mineral, the polymer and the micellar solution.

Conclusions

It is shown that aqueous dispersions of a synthetic clay mineral are transformed by amphiphilic water soluble polymers like PVA into soft gels. The polymer binds on the clay mineral and the adsorbed coils act like crosslinking agents between the clay mineral particles. The resulting gels have a yield stress value and a frequency independent storage modulus. Under saturation the clay

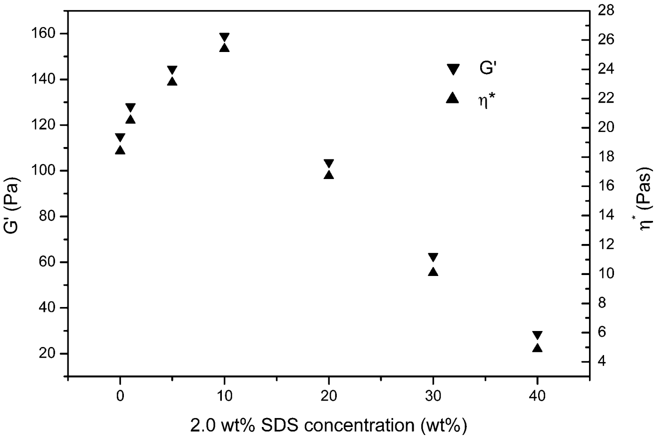

Fig. 13 Effect of 2.0 wt% SDS concentration on elastic modulus and complex viscosity of gel of 2.0 wt% SKS-20/2.0 wt% PVA 2 (9:1)

mineral particles can adsorb the fivefold weight of PVA of their own weight. Anionic surfactant adsorbs on PVA and renders it hydrophilic. As a consequence PVA can no longer bind to the clay mineral and the gels are transformed to low viscous aqueous solutions.

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