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SHORT COMMUNICATION

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A shear-induced viscoelastic system through addition of a crown-ether to AOT w/o-microemulsions

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Abstract Addition of the crown-ethers 15-crown-5 (CE5) and 18-crown-6 (CE6) to Aerosol OT (AOT)-stabilized w/o microemulsion leads to drastic rheological changes.

A mixture of 20 wt% solution of a CE in water with an oil stock solution of AOT is biphasic but can be transformed into a homogeneous, transparent, viscoelastic solution by simple shaking. This gelly phase demixes again after hours up to several days. In addition, anomalous percolation properties are found for mixtures containing small amount of CE. Both effects are interpreted taking into account the complexing ability of the CEs with respect to the sodium counterion of AOT.

Key words Mircoemulsions – percolation – viscoelastic gel – rheology – conductivity

Introduction

The phase behavior of w/o microemulsions consisting of water dispersed in a majority phase of an oil stabilized by an ionic or non-ionic surfactant has been extensively studied [1]. Most of these systems exhibit a steep increase in electrical conductivity of some orders of magnitude by changing the temperature from the solubilization- to haze-boundary. This process is generally called a percolation transition and we use this term irrespective of the underlying mechanism of electrical conduction, which is controversially discussed in the literature [2, 3].

The effect of additives on the phase and percolation behavior of microemulsions has been the subject of interest in recent publications [4, 5]. By far the largest specific effects [6] are observed adding electrolytes to ionic microemulsions. In general, experiments show that added salts stabilize droplets against temperature- and volume-fraction-induced percolation, while most small organic solutes induce the percolation transition, regardless of whether ionic or non-ionic amphiphiles are used. One exception is ethylene glycol inducing percolation in ionic AOT systems (as other hydrophillic alcohols do) but stabilize droplets in the non-ionic IG system. An attempt to explain this behavior has been made recently [7] in a paper regarding the influence of oligo- and polyethylene glycols on microemulsions. In order to complete these investigations, the effect of two cyclic analogues of the oligoethylene glycols, the crown-ethers 15-crown-5 and 18-crown-6, on AOT and IG microemulsions has been examined.

Experimental

Materials

Sodium bis-2-ethylhexylsulfosuccinate (Aerosol OT, AOT) was purchased from Sigma and Igepal CO-520 (4-nonylphenyloligoethylene glycol, IG) from Aldrich and used as received. The different alkanes were obtained from Merck in analytical grade. 15-crown-5 (CE5) was purchased from Merck and 18-crown-6 (CE6) from Sigma. The composition is characterized by the molar surfactant concentration in oil, the weight fraction Y of additive in water, and W_0^* defined as

$$W_0^* = \frac{V(\text{polar})}{n(\text{surf.})M(\text{H}_2\text{O})/\rho(\text{H}_2\text{O})} \quad (1)$$

where V(polar) is the volume of the polar phase and $M(H_2O)$ and $\rho(H_2O)$ are the molar mass and the density of water, respectively. For pure water as polar phase, W_0^* equals the molar water to surfactant ratio W_0.

Methods

Temperature-dependent conductivities were measured with a Tinsley Prism LCR databridge at a frequency of 1 kHz using a WTW-LTA 1 electrode. The percolation thresholds are obtained from the point of inflection of the logarithmic conductivity vs. temperature curve. Viscosity measurements were performed with a thermostated rotation viscosimeter (Physica SM) using a double gap measuring system with a shear rate range γ from 5.04 s^{-1} up to 4031 s^{-1}.

Results

The specific shift of the percolation threshold to lower temperatures in ionic AOT microemulsions due to addition of oligoethylene glycols is comparable to the effect of small organic compounds like hydrophillic alcohols or ureas and is in the range of 0.5 °C/wt% additive. The addition of 18-crown-6 (= cyclohexaethylene glycol) causes a specific shift of more than 8 °C/wt%, as can be seen in Fig. 1.

Substitution of 20% water in an AOT system with $W_0^* = 55.5$ by linear oligoethylene glycols and by cycloethylene glycol, respectively, leads to completely different behavior. The system with the linear additive is an one-phase low-viscosity mircoemulsion with phase boundaries and percolation temperature shifted about 10 °C to smaller values with respect to the additive-free microemulsion. The crown-ether system is biphasic in the thermodynamic equilibrium. But shaking the sample or even sucking it into a pipette results in a system with anomalous behavior. It turns out that forced by a low shear stress the system thickens to a homogeneous nearly transparent gelly phase which relaxes slowly after termination of shaking. A system of two immiscible low-viscosity fluids is reached only after days.

Adding a solution of 20 wt% of CE6 (or CE5) in water to a stock solution of AOT in different oils shows that a critical minimum W_0^* value of about 50 is necessary to produce the gelly phase by simple shaking. This value is independent of the oil (decaline, *n*-heptane, *n*-octane, *n*-decane were used), unaffected by the molar surfactant concentration in oil $C_{\text{surf.}}$ (0.1–0.3 M), and independent of the temperature. It is equivalent to an AOT to crown-ether molar ratio of about 1.

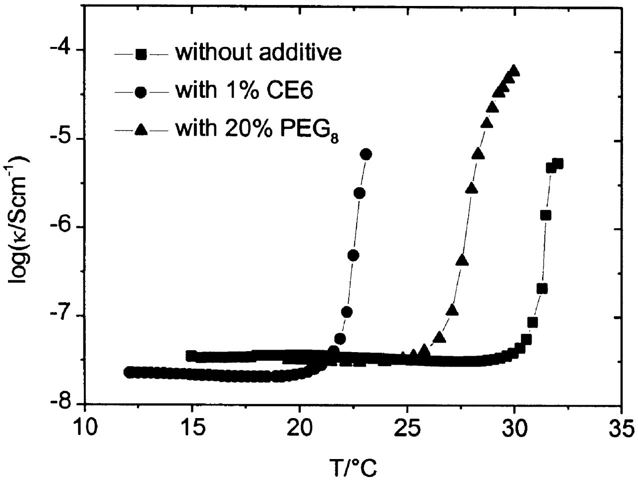

Fig. 1 Conductivity vs. temperature in an AOT microemulsion ($c = 0.1$ M AOT in *n*-heptane, $W_0^* = 55.5$) without additive (■), with 1 wt% 18-crown-6 (●), with 20 wt% EG_8 (▲) in the polar phase

The gelly phase is electrically conducting over the whole temperature range. It breaks down under addition of salt, when a salt to CE molar ratio of about 1 is reached. The gel also collapses directly under ultrasonification.

Viscosity measurements were performed to characterize the gelly phase. The logarithmic plot of the viscosity as a function of time (Fig. 2) shows that the system is thixotropic. The relaxation can be described by at least two exponential processes with time constants of 50 and 300 min, respectively. Higher shear rates as used in the previous experiment lead to a collapse of viscosity reaching a constant viscosity of about 10 mPa s for $\gamma > 300\,s^{-1}$ which is in the range of the additive free microemulsions at low shear rates. The viscosity can be alternately switched within 90 s between the high value of about 3 Pa s and the low one of about 10 mPa s by changing the shear rate from 5 to 500 s^{-1} and back.

In the non-ionic IG system, the resulting effect of CE addition is identical to the influence of the linear oligoethylene glycols. The effect of cyclic CE6 corresponds to a linear oligomer with a degree of polymerization of about 4.5, as can be seen from the linear part of the molecular weight dependence of the percolation

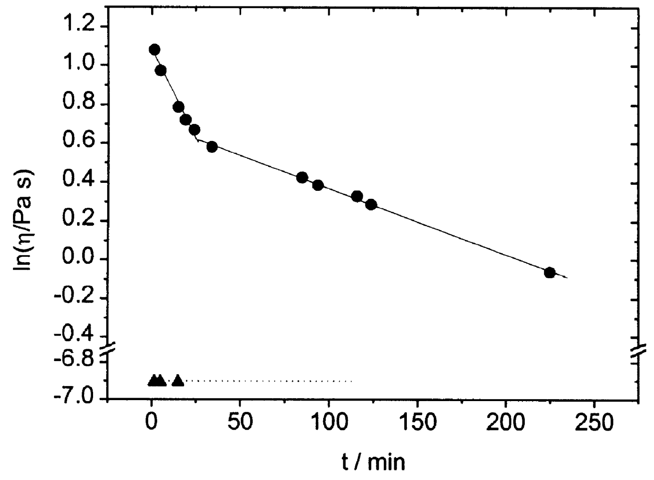

Fig. 2 Viscosity of the gelly AOT system under small constant shear ($\gamma = 5.04\ s^{-1}$) (●) and high constant shear ($\gamma = 504\ s^{-1}$) (▲), respectively, at a temperature of 28.0 °C as a function of time. System: AOT/*n*-decane/20% CE6 in water; $W_0^* = 55.5$, $c_T = 0.1$ M. At $t = 0$ the system has been switched in each case from the opposite of both shear rates

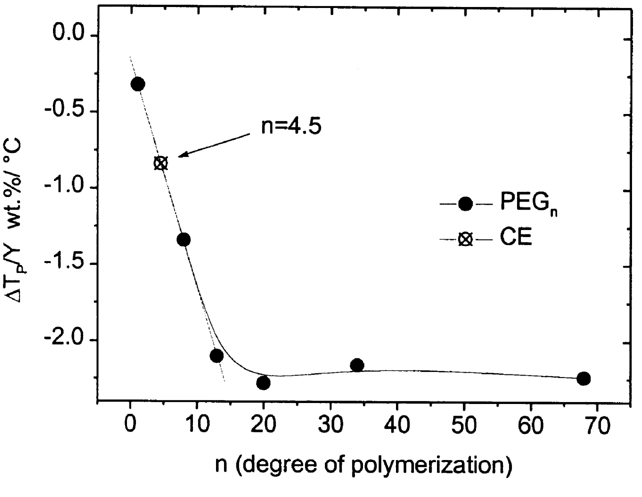

Fig. 3 Specific percolation temperature shift in an IG system ($c_T = 0.19$ M in *c*-hexane, *n*-hexane (1:1); $W_0^* = 10.0$) containing oligoethylene glycols as a function of the degree of polymerization. 18-crown-6 can be incorporated with $n = 4.5$

temperature shift (Fig. 3). The percolation curves become less steep with increasing CE concentration and the absolute conductance in the percolated regime is remarkably decreased (Fig. 4.)

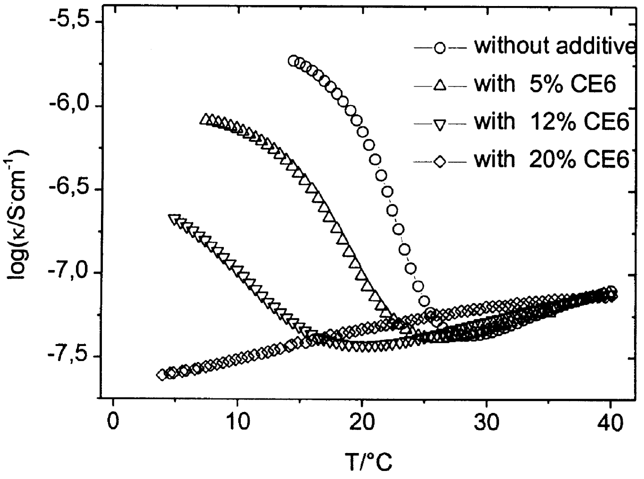

Fig. 4 CE in IG microemulsions. Temperature dependent electrical conductivities for an IG system (as in Fig. 3) with different CE6 concentrations

Discussion

The magnitude of the crown-ether effect on AOT microemulsions is much bigger than the effect of usual polar organic compounds. Therefore, it cannot be due to a simple interaction of glycol monomer units with the surfactant layer. It is in the range of a salt effect but of opposite sign.

Cyclic ethers as, e.g. 18-crown-6 are known for their ability to complex ions. Small, single-charged cations fit properly into the core of CE5 and CE6. Probably, both the large influence on the percolation behaviour and the shear-dependent and thixotropic viscosity are due to the formation of a complex between the crown-ether and the sodium ion of AOT.

The stabilizing effect of salts on ionic microemulsions is discussed in terms of a decrease in the repulsive interaction between the surfactant headgroups due to the increased ionic strength. On the other hand removing of counterions from the surfactant layer by complexation should show a similar large effect of opposite sign, and an effect like this can be seen in the case of crown-ether addition. The effect of Kryptofix 222 on AOT microemulsions has also be discussed in terms of its complexing ability [8].

Salt addition has no large influence on non-ionic microemulsions beside the absolute conductivity in the percolated regime. The fact that CE behaves as a linear oligoethylene glycol in the IG system therefore is in line with an interpretation of a reverse salt-effect in ionic systems. However, the influence of CE on charge carriers can also be seen in the IG system (Fig. 4). Charged impurities of IG which are responsible for the relatively high conductivity in the percolated regime are forced into complexes resulting in significantly lower conducting microemulsions in the percolated regime. The number of charge carriers is not changed. The decreased conductivity thus monitors a restricted mobility of the charge carriers in the complexed form. This might be due to only small channels between electrically isolated but aggregated droplets even in the percolated regime. Another explanation of the decreased mobility can be large attractive forces between the complex and the surfactant layer resulting in adsorption.

The formation of viscoelastic transparent fluids by vigorous shaking has been observed earlier in water/oil/surfactant systems [9]. The high viscosity is there attributed to the formation of extended structures, e.g. entangled worm-like micelles. Due to shear forces the attractive forces leading to phase separation seem to be reduced. Additionally, the structure of the CE system is water continuous as indicated by the high electric conductivity over the whole temperature range.

Changing rheological properties of ionic surfactant systems by simple addition of complexing agents as crown-ethers may find applications in designing special colloidal suspensions. The potential of drastic influence on the phase behaviour by small CE amounts can be useful for the sensitive control of reaction conditions in microemulsions, e.g. for polymerization processes.

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