Hydrophobically cross-linked micellar solutions : microstructure and properties of the solutions

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Résumé. – Nous avons étudié le phenoméne d´aggregation du composé ramifié dioleyl - polyethyleneoxide (R (-EO-)$_x$ R, avec x = 55, 90, 135) avec et sans la présence des goutelettes O / W microémulsion globulaire. Les goutelettes se composaient de tetradecyldimethylaminoxide et de decane et avaient un rayon de 33 Å environ. Il est apparu que l´agent ramifiant a une cmc bien défini et forme des micelles. Le nombre d´aggregation fut déterminé par diffusion de lumière et se situe environ vers 20 - 30. Par diffusion des neutrons aux petits angles (SANS) des nombres d´aggregation un peu plus grand furent obtenus. Des mesures rheologigues montrèrent une ramification à des concentrations plus elevées. L´agent ramifiant fut ajouté à des solutions qui contenaient des goutelettes de microémulsion. On a observé que la viscosité des ces solutions pouvaient été considérablement élevée par addition de cet agent ramifiant. Les études en SANS et en diffusion de lumière ont prouvé que la taille des goutelettes ne change pas. Les valeurs expérimentales des micelles ramifiés peuvent étre décrites par le modèle d´une sphère dure comprenant en plus un potentiel terme d´attraction. Les modules de cisaillement déterminés à partir de solutions viscoélastiques sont en accord avec ceux determinés par diffusion.

Abstract. – The aggregation behavior of the cross - linking agent dioleyl – polyethyleneoxide (R (-EO-)$_x$ R, with x = 55, 90, 135) with and without the presence of globular O / W microemulsion droplets was investigated. The microemulsion droplets consisted of tetradecyldimethylamine oxide (TDMAO) and decane and had a radius of about 33 Å. It was found that the cross - linking agent has a well defined cmc and forms micelles. The aggregation number was determined by light scattering measurements and lay in the range of 20 - 30. From SANS measurements somewhat higher aggregation numbers were obtained. Rheological measurements showed that the systems cross - link at high concentrations. The cross - linking agent was added to solutions that contained microemulsion droplets. It was found that the viscosity of these solutions could become significantly enhanced upon its addition. SANS and light scattering data of these solutions showed that the size of the droplets did not change. The scattering data of the cross - linked micelles could be fitted with a model for hard spheres that included an additional attractive term. The shear moduli which were determined from the viscoelastic solutions are consistent with the scattering data.

Introduction

In many colloidal formulations it is general practise to add thickeners to control the flow behavior of the systems. Standard thickeners are water soluble polymers with a large molecular weight of several million Dalton. Under these condition the effective volume of the coiled polymer can be hundred times larger than the real volume and as a consequence the coils overlap even when the thickener is added in small concentrations of less than 1 wt %. Solutions with overlapping coils always display a much higher viscosity than the solvent [1, 2].

The thickening effect of water soluble polymers can be increased if the polymer is hydrophobically modified [3 - 5]. Very effective thickeners are obtained when polyelectrolytes are hydrophobically modified [6 - 10]. Usually only a few percent of the monomers from which the polyelectrolytes are formed have to be replaced by monomers with *alkylgroups* having a chainlength typical for surfactants. The same principle has also been applied to water soluble polyacrylamide [11 - 13] and to water soluble hydroxyethylcellulose [14 - 18]. Aqueous solution of such compounds with 1 wt % may have viscosities which are 10^5 times higher than that of water.

The increased thickening effect of these compounds is a result of the formation of cross - links between the individual molecules. The polymers *form a three* dimensional network in which the network points consist of aggregated alkylchains. The alkylgroups of the polymers can also interact with other colloidal particles which have a hydrohobic surface or interior. In this way the cross - linking effect of the thickening agent will be even larger.

Because of the complicated structure of the agents, in such systems it usually is very difficult to determine the degree of inter- and intra-molecular *cross - linking*. Very few data are therefore available on the microstructure of these systems. In this investigation we will study very simple cross-linked model systems. The cross-linking agent is polyethyleneoxide (PEO) of various degree of polymerization with two alkylgroups at both ends. The chemical structure of these compounds resembles that of hydrophobically modified ethoxylate urethanes (HEUR), a class of substances that has been intensively investigated with respect to its influence on the rheology of *surfactant* systems [19, 20]. The compounds will be used to cross - link low viscous solutions of O / W (oil in water) microemulsion droplets. In this situation the concentration of the droplets and the cross - linking agent can be adjusted in such a way that each solution on its own has a low viscosity and that there are no cross - links.

1. Materials and Methods

As thickeners dioleylpolyethyleneoxide compounds $R \dashv EO \dashv_x R$ with a length of the polyethyleneoxide (PEO) part of x = 55 (CL 428), 90 (CL 632), or 135 (CL 633) were employed. These compounds were received as a gift from Th. Goldschmidt AG with a distribution of the length of the polyethylene unit with x being the average degree of polymerization. Dimethyltetradecylamineoxide (TDMAO) was obtained from Hoechst and recrystallized twice in Acetone before used.

Table 1: Molecular weight $\bar{M}_w$, and mean degree of polymerization $\bar{x}$ for the dioleylpolyethyleneoxide compounds $R \dashv EO \dashv_x R$

compound	R	$\bar{M}_w$ in g / mol	$\bar{x}$
CL 428	Oleyl	3120	55
CL 632	Oleyl	4570	90
CL 633	Oleyl	6570	135

Surface tension measurements were carried out by means of the ring method (Lauda - Tensiometer). Light scattering data were obtained with a Laser light scattering instrument (Chromatix KMX 6) that allows for a measurement at a scattering angle of 6°. The refractive index increments d n / d c were determined with the KMX - 16 instrument from Chromatix. The SANS experiments were carried out at the KFA in Jülich. Rheological measurements were performed with the fluid rheometer RF 7000 (Rheometrics) for solutions of high viscosity and with a Paar OCR - D oscillatory capillary viscosimeter for the ones of low viscosity.

2. The pure thickening agent

2.1 Surface tension — CMC

The two thickening compounds with the longest PEO units, i. e. CL 632 and CL 633, are soluble in water and they display surface active behavior at the water / air interface. This property was investigated by means of surface tension measurements and the surface tension σ as a function of the concentration is shown in fig. 1. In both cases the typical behavior of self – aggregating surface active compounds is observed, which means that the surface tension σ first decreases linearly with ln c and then remains constant at higher concentrations. In this process σ is reduced to 41 mN / m for the CL 632 and to 40 mN / m for the CL 633. The critical micellar concentration (cmc) of the thickening compounds can be deduced from the point of the discontinuity in the σ (ln c) curve. For the CL 632 a cmc value of $6.3 \cdot 10^{-3}$ wt % (= $1.38 \cdot 10^{-5}$ mol / l) and for the CL 633 one of $9.1 \cdot 10^{-3}$ wt % (= $1.39 \cdot 10^{-5}$ mol / l) was obtained. On a molar basis the cmc values are almost equal which is not too surprising because it should mainly be determined by the hydrophobic part of the surface active agent, which in both cases consists of the oleyl chain. From the initial slope (dσ / d ln c) of the curves the head group area per molecule A can be calculated by means of the Gibbs equation (eq. 1):

$$A = \frac{k \cdot T}{(d\sigma / d \ln c)} \tag{1}$$

By using this equation a value of 68 and 48 A^2 can be obtained for CL 632 and CL 633, respectively. Here the compound with the shorter PEO chain requires a larger area per molecule at the interface. The reason for this might be that with the shorter PEO unit the possible configurations of the amphiphile are significantly more restricted and therefore it is more difficult for the molecule to accomodate the two hydrophobic moieties at the interface, which requires a larger area for the individual oleyl end groups.
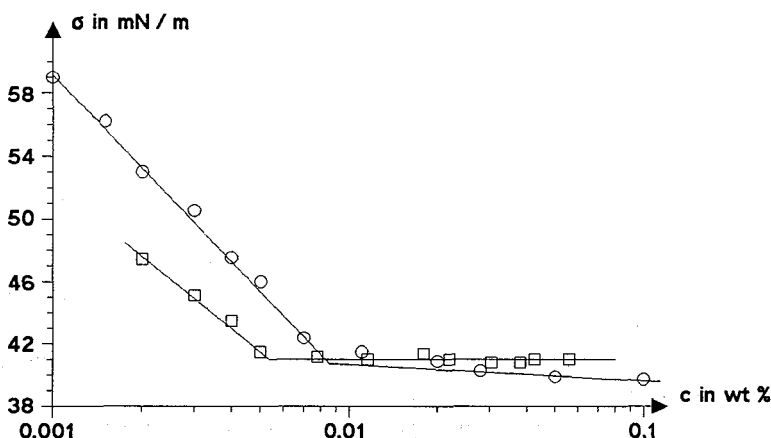

Fig. 1: Surface tension σ as a function of the concentration for CL 632 (□) and CL 633 (○)

2.2 Light scattering data

In fig. 2 static light scattering data of the two studied systems of pure thickening agents CL 632 and CL 633 are depicted. For comparison also the scattering data for the microemulsion droplet system composed of TDMAO and decane (molar ratio of TDMAO / decane = 3.2 : 1) is shown which has been studied in detail before [21, 22] and which will later be used for the cross – linking experiments. The droplets in
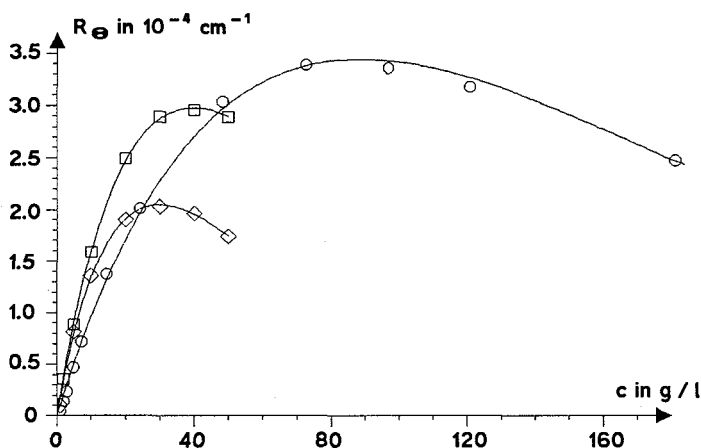
Fig. 2: Rayleigh ratio $R_{\ominus}$ at 25 °C as a function of the concentration for : $\bigcirc$: x (TDMAO) / x (decane) = 3.2 : 1; $\square$: CL 632; $\Diamond$: CL 633. Solid lines are the fitted theoretical curves according to the Carnahan – Starling expression.

this system behave almost like ideal hard core particles in scattering experiments. This can directly be infered from the scattering maximum which occurs around 13 wt %. Therefore it was attempted to describe the experimental data by a simple hard sphere model. The Rayleigh ratio in light scattering is given by eq. 2, where the particle form factor $P(\ominus)$ accounts for the intraparticle interferences and $S(\ominus)$ for the interparticle interferences. Because the aggregates here are much smaller than the wavelength of light and the scattered intensity was recorded at a scattering angle $\ominus$ of 6^{0} one may well assume the scattering to occur in the limit of very small wave vectors q (eq. 3), i. e. q · R << 1. In that limit $P(\ominus)$ assumes the constant value of one and for the structure factor its limiting value $S(0)$ may be used, i. e. the scattering intensity is determined by the osmotic compressibility of the system [23]. For a hard sphere system the Carnahan – Starling [24] formula (eq. 4) is known to describe the structure factor $S(0)$ very accurately even for very high volume fractions. With this expression for $S(0)$ inserted in eq. 2 we fitted the experimental data under the *assumption* of a constant particle size and hence of the molecular weight of the respective aggregates for the whole concentration range investigated. This model uses two fit parameters, the particle radius R_{0} as derived from the molecular weight via the particle density (0.851 g / mol for the TDMAO / decane system as obtained from density measurements) and its hard sphere interaction radius R_{s} as derived from the effective volume fraction Φ_{eff} as compared to the volume fraction of surfactant *plus* hydrocarbon Φ_{E}. The theoretical curve for the parameters given in table 2 is shown in fig. 2 as solid line and in good agreement with the experimental data. In this model the interaction radius R_{s} is about 2.5 Å larger than the particle radius R_{0} which corresponds to a very reasonable value for the thickness of the hydration shell of the aggregates. The good agreement also confirms the validity of the assumption that the microemulsion droplets retain their size irrespective of the total *concentration.*

The cross – linking compounds CL 632 and CL 633 also give a maximum after a more or less linear increase. The maximum is now shifted to much smaller concentrations. This immediatly shows that the effective volume of the aggregates should be about 3 - 4 times larger than their real volume. Again the experimental scattering data were analyzed with the simple hard sphere model described above and as in the case of the microemulsion droplets an excellent agreement between the theoretical and experimental values can be observed (fig. 2). From the values of the fit parameters in table 2 it can be seen

that the effective hard sphere volume of the aggregates is 3.25 and 4.32 times larger than their dry' volume for the CL 632 and CL 633 system, respectively, which means that their hard core radius is about 1.5 times larger that the radius which a compact sphere of the compounds would have. This increase of the effective volume fraction has to be attributed to the hydration of the ethoxy groups and also to the fact that the hydrophilic PEO chains protrude far out into the solution surrounding the hydrophobic part of the aggregates which results in a mutual repulsion of the particles. Therefore it is easy to understand that this effect is more pronounced for the CL 633 with its longer PEO unit than for the CL 632. In dilute solutions the aggregates would thus have to look like the model shown in fig. 3 a, i. e. isolated, unconnected micellar aggregates with a relatively large shell of hydrated PEO chains surrounding a hydrophobic core.

$$R_\Theta = \frac{4 \cdot \pi^2 \cdot n^2}{N_A \cdot \lambda^4} \left(\frac{dn}{dc}\right)^2 c_g \cdot M_w \cdot P(\Theta) \cdot S(\Theta) \qquad (2)$$

n: refractive index
dn/dc: refractive index increment
N_A: Avogadro constant
$P(\Theta)$: particle form factor (accounts for the intraparticle interferences)
$S(\Theta)$: structure factor (accounts for the interparticle interferences)

λ: wave length
c_g: concentration (in mass / volume)
M_w: molecular weight

$$q = \frac{4 \cdot \pi \cdot n}{\lambda} \sin(\Theta/2) \qquad (3)$$

$$S(0) = \frac{(1-\Phi)^4}{(1+2\Phi)^2 - 4\Phi^3 + \Phi^4} \qquad (4)$$

Φ: effective volume fraction

Table 2 : Particle radius R_0, ratio of effective hard sphere volume fraction to the volume fraction of the nonaqeous compounds Φ_{eff}/Φ_E, hard sphere interaction radius R_s, and aggregation number of the amphiphile N_{Agg}.

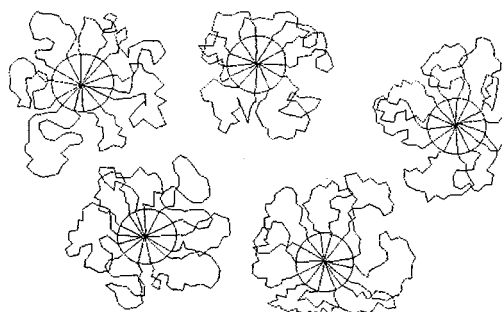| system	R_0 in Å	Φ_{eff}/Φ_E	R_s in Å	N_{Agg}	M_w in g / mol
TDMAO + Decane	31.8	1.26	34.3	230	$6.87 \cdot 10^4$
CL 632	38.3	3.25	56.8	31.0	$1.42 \cdot 10^5$
CL 633	37.6	4.32	61.2	20.4	$1.34 \cdot 10^5$

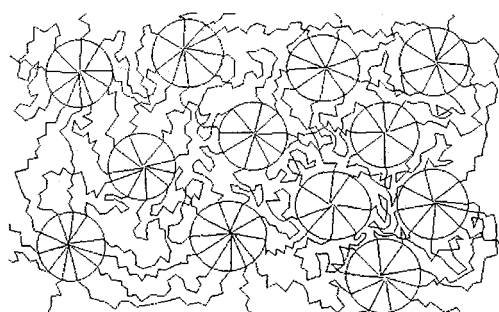Fig. 3 a : Schematic drawing of the situation in the dilute region.

Fig. 3 b : Schematic drawing of the situation in the concentrated region.

2.3 SANS

Unfortunately only very few SANS data on the solutions of the thickener are available and these data were obtained on solutions with a rather high concentration of 10 wt % where there is considerable interaction between the coils. The scattering intensities as a function of the momentum transfer q are shown in fig. 4. As expected a strong correlation peak can be observed. By the position q_{max} of this intensity maximum the mean distance d between the aggregates is given as $d = 2\pi / q_{max}$. Now the size of the aggregates may be concluded from this mean distance and the knowledge of the volume fraction ($\Phi = 0.109$). If one assumes every particle to be placed in a box with edges of length $2\pi / q_{max}$ then in this simple approximation the radius of the aggregates should be given by eq. 5.

$$R = \sqrt[3]{\frac{3 \cdot \Phi}{4 \cdot \pi}} \; \frac{2 \cdot \pi}{q_{max}} \tag{5}$$
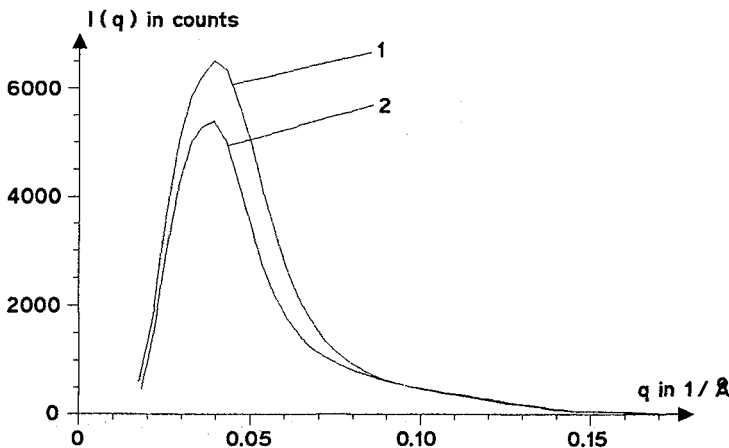

I(q) in counts

q in 1 / Å

Fig. 4 : SANS intensity for a 10 wt % solution of CL 632 (1) and CL 633 (2) in D_2O.

The radii computed this way (table 3) are considerably larger than those obtained from the light scattering data, which translates into aggregation numbers roughly twice as large. It is likely that the increased aggregation numbers are due to intermicellar cross-linking. At 10 wt % the intermicellar distance is now so small that some molecules may cross-link the micelles. This releases some strain in the packing of the micelles and they now can grow larger. The situation which we think exists now in the solution is sketched in fig. 3 b.

Table 3 : SANS data : q-value for the scattering maximum q_{max}, particle radius R, and aggregation number N_{Agg} (both deduced from q_{max}).

10 wt %	q_{max} in 1 / Å	R in Å	N_{Agg}
CL 632	0.0395	47.1	57.7
CL 633	0.0380	49.0	45.2

2.4 Rheological data

From the sketch which is shown in fig. 3 b we can expect a network-type with transient cross-links for the more concentrated solutions. The structural time constant for such a network should be determined

by the dissociation process of an oleyl chain leaving the micelle. The time constant for such a kinetic process can be estimated and compared with the measured structural relaxation time τ_s of the oscillatory shear experiments, which is related to the rheological properties via eq. 6.

$$G_0 = \eta_0 \cdot \tau_s \qquad\qquad (6)$$

However the kinetic time constant for the dissociation process may be estimated by a simple approximation. The process of micelle formation can be described by a sum of single association – dissociation processes according to eq. 7, i. e. a step – wise micellar association [25]. Now one may assume the equilibrium constant K (and therefore the kinetic constants k^+ and k^-) to be fairly independent of the aggregation number s. With this assumption one can conclude that K should be approximately equal to the inverse of the cmc (eq. 8) because at this point $c(A_{S-1})$ and $c(A_S)$ should be identical and still much smaller than the monomer concentration $c(A_1)$. Now the kinetic constant for the dissociation process k^- is given according to eq. 9 and directly related to the time constant τ for this process by eq. 10 where the factor 2 is required because every molecule contains 2 hydrophobic oleyl chains. Usually the rate constant k^+ for the association step is diffusion controlled and in the range of 10^9 l / mol $\cdot$ s [26]. If one now takes such a value, uses the cmc as given in 2.1 and the aggregation number according to table 2 one arrives at values for τ of 3 – 5 ms. These values correspond well with the experimental values for the structural relaxation time τ_s which were determined to be in the range of 1 – 8 ms from oscillatory rheological measurements. From this close correspondence it may be concluded that the structural relaxation time is determined by the dissociation rate of the oleyl groups leaving the aggregate, i. e. the structural relaxation time is kinetically controlled [27].

$$A_{S-1} + A_1 \underset{k^-}{\overset{k^+}{\rightleftharpoons}} A_S \qquad\qquad (7)$$

$$K = \frac{k^+}{k^-} = \frac{c(A_S)}{c(A_{S-1}) \cdot c(A_1)} \approx \frac{1}{cmc} \qquad\qquad (8)$$

$$k^- = k^+ \cdot cmc \qquad\qquad (9)$$
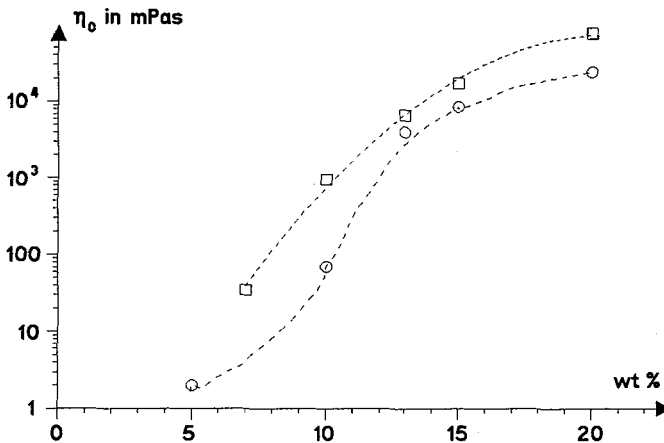
$$\tau = \frac{1}{(k^- / 2 \cdot N_{Agg})} \qquad\qquad (10)$$

Fig. 5: Zero – shear viscosity η_0 as a function of the concentration for the CL 632 ($\square$) and CL 633 ($\bigcirc$) system at 25 °C.

In fig. 5 the zero-shear viscosities η_0 of the CL 632 and CL 633 solutions are presented. Here one ob-
serves a strong increase of the viscosities at around 6 wt % and then a more or less continuous in-
crease with c in the semilogarithmic plot. The high viscosities of the more concentrated samples are
consistent with a picture of cross-linked micellar aggregates as they are sketched schematically in
fig. 3 b. At this concentration the mean distance between the micelles becomes small enough so that the
cross-linking agents can anchor their alkylgroups in two neighboring micelles and bridge the gap. This
would explain the high viscosities and also the elastic properties, i. e. the high shear modulus of the re-
spective samples. It is interesting to note that the viscosities for the CL 632 are always somewhat hig-
her than those of the CL 633, the compound with the longer PEO chain. At first this might look a little
bit surprising because according to the light scattering results (2. 2) the CL 633 has the larger effective
volume fraction at the same concentration and should therefore also show a larger viscosity. But this
would only be true if the viscosity resulted from individual aggregates trying to pass each other. However
here this very high viscosity is the result of cross-linked hydrophobic aggregates and because their size
is approximately the same for CL 632 and CL 633 the number density of the aggregates will be higher
for the CL 632 with its relatively larger hydrophobic part. Therefore also the number density of the
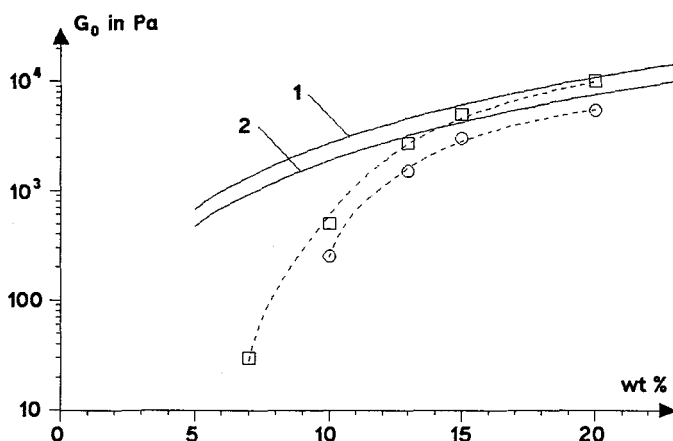cross-links ought to be higher which explains the higher viscosity.

Fig. 6 : Shear modulus G_0 as a function of the concentration for the CL 632 (□) and CL 633 (○) system
at 25 °C. (solid lines : theoretical curve calculated according to : $G_0 = v \cdot k \cdot T$; for CL 632 (1) and
CL 633 (2))

The shear modulus G_0 could be measured for the more viscous solutions and the results are shown in
fig. 6. The value of G_0 is always in the range of 0.2 - 20 kPa and again one finds somewhat larger values
for the compound with the shorter PEO unit (CL 632). In a simple network theory the modulus G_0 should
depend on the number density v of elastically effective chains between the cross-links via [28] :

$$G_0 = v \cdot k \cdot T \qquad\qquad (11)$$

Here the upper limit of the number density v should simply be given by the number density [1]N of the
cross-linking molecules, but in reality not every molecule will bridge two aggregates. The probability that
one molecule being anchored in a certain aggregate will have its other oleyl group in a different aggre-
gate may in a simple approximation be estimated to be equal to the volume fraction Φ of the aggregates.
With this assumption the shear modulus may be expressed by eq. 11 a.

$$G_0 = {}^{1}N \cdot \Phi \cdot k \cdot T \qquad\qquad (11\,a)$$

With this expression (and assuming that the density of the solutions does not differ significantly from that of water, which has been verified by density measurements) a theoretical shear modulus of the corresponding systems, i. e. CL 632 and CL 633, could be calculated. The calculated values are plotted as solid lines in fig. 6 and are in fairly good agreement with the experimental data for the samples of high concentrations, where one would expect the process of cross-linkage to be effective. Therefore this very crude model of cross-linked aggregates already allows for a reasonble prediction of the mechanical properties of the respective system.
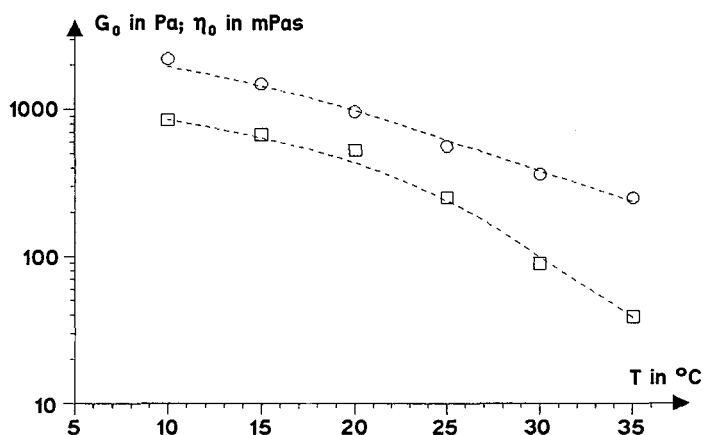

Fig. 7: Shear modulus G_0 (□) and zero-shear viscosity η_0 (○) as a function of the temperature for a 10 wt % solution of CL 632 in water.

The viscosity of concentrated solutions depends very much on the temperature. Both the zero-shear viscosity and the shear modulus decrease strongly with increasing temperature. This effect is shown in fig. 7 for a 10 wt % solution of CL 632. Within our model of cross-linked micelles the decrease of the viscosity η_0 could be caused by a shortening of the structural relaxation time τ_s or a decrease of the shear modulus G_0 (compare eq. 7). However it was found experimentally that the decrease of viscosity and shear modulus runs almost parallel. From this it can be concluded that the structural relaxation time τ_s does not change significantly with temperature and that it is the shear modulus which causes the diminution in viscosity.

This result can easily be explained. It is known that the solubility of the ethoxy groups is weakened with increasing temperature. As a result alkylethoxylates become more lipophilic with increasing temperature. This usually leads to larger aggregation numbers and to a more condensed layer of the ethoxy groups surrounding the micelles. As a consequence it seems that the compounds can no longer bridge the intermicellar gap and the system switches gradually back to an uncross-linked state.

3. Results for the cross-linked microemulsion droplets

3.1 Light scattering and SANS-data

Solutions of TDMAO which contain some solubilized hydrocarbon, i. e. the L_1-phase, have been studied in detail before [21, 29]. From static light scattering experiments and SANS measurements it could be concluded that solutions with an amount of decane close to the solubilization capacity contain rather monodisperse spherical particles with a hard core radius of ∼ 33 Å [29]. The dimension of the droplets are independent of the total surfactant concentration when the surfactant / hydrocarbon ratio is kept constant.
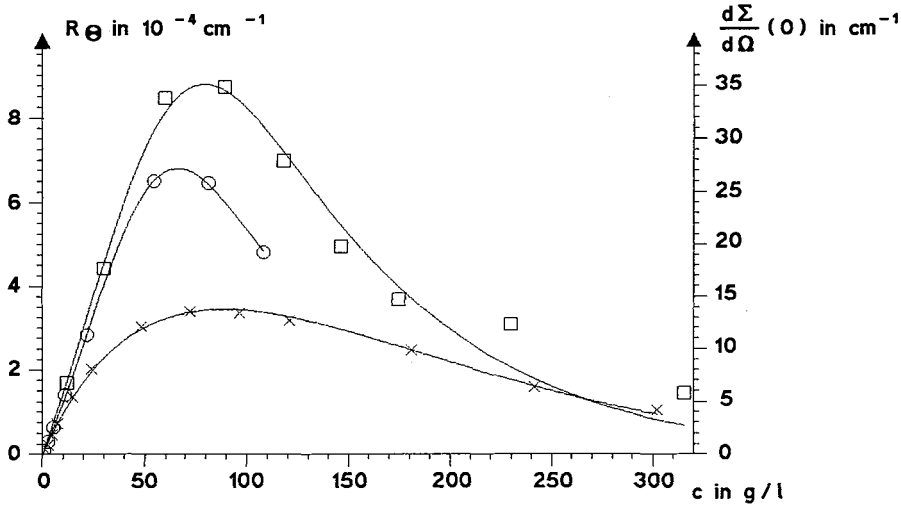
Fig. 8 : Rayleigh ratio R_Θ (O) and SANS differential cross section $d\Sigma / d\Omega$ ($q \to 0$) ($\square$) as a function of the total concentration (surfactant plus decane) for the microemulsion system with 10 wt % (relative to TDMAO plus decane) CL 428 (at 25 °C). For comparison R_Θ for the pure TDMAO system (x). (solid lines : fitted curves)

In the following experiments we therefore kept the surfactant / hydrocarbon ratio and also the ratio of the cross – linking agent to the surfactant constant (at m (TDMAO) / m (decane) = 5.4 : 1; m (CL 428) / m (TDMAO + decane) = 1 : 10). Static light scattering experiments were only performed on solutions up to 10 wt % because of the high viscosity of the more concentrated samples. SANS measurements were done in D_2O and here we have given the scattering intensity as extrapolated to zero scattering vector, which should be equivalent to the light scattering data. The light scattering and the SANS data show again a maximum with increasing volume fraction Φ of the system which occurs approximately at the same volume fraction as for the solutions without the cross links. The intensity at the concentration of the scattering maximum is however higher as in the solution without the cross – linking agent, which is also shown in fig. 8 for a comparison. This seems to indicate that the aggregates have become larger. However this is not the case. The increased intensity is a result of a changed interaction potential. In the case of the pure TDMAO / decane system the scattering data could very well be described with a simple hard sphere model (compare 2. 2) as can be seen by comparing the experimental data with the theoretical values (solid line in fig. 8). Yet the scattering data for the system containing the CL 428 could not at all be described satisfactorily with the hard sphere model.

In order to overcome this discrepancy a model was used that includes an additional attractive potential term [30] and which has been employed successfully before for the analysis of scattering data from W / O microemulsions [31 - 33]. According to this perturbation theory such an attractive potential results in a first order approximation in an additional term π_A for the osmotic pressure of the system (eq. 12). Here the parameter A is directly related to the interaction potential U (r) of the particles via eq. 13. From this definition it is evident that A has to be closely related to the second virial coefficient B_2 and this relation is given by eq. 14, where the ratio Φ_{HS} / Φ takes into account that the effective hard sphere radius of an aggregate may differ from its real radius. Now the osmotic compressibility is directly related to the structure factor of the respective system [34] and using this model one obtains eq. 15 for the structure factor S (0) of such a system with an additional attractive potential term.

$$\pi_A = \frac{k \cdot T}{V_A} \frac{A}{2} \Phi^2 \qquad\qquad\qquad (12)$$

V_A : volume of the aggregate

Φ : volume fraction

$$A = \frac{4 \cdot \pi}{V_A} \int_{2R_{HS}}^{\infty} (1 - \exp(U(r)/k \cdot T)) \, r^2 \cdot dr \qquad\qquad (13)$$

$$B_2 = 4 \cdot (\Phi_{HS}/\Phi) + A/2 \qquad\qquad\qquad (14)$$

Φ_{HS} : effective hard sphere volume fraction (results from the hard sphere interaction radius)

$$S(0)^{-1} = \frac{(1 + 2\Phi_{HS})^2 - 4 \cdot \Phi_{HS}^3 + \Phi_{HS}^4}{(1 - \Phi_{HS})^4} + A \cdot \Phi \qquad\qquad (15)$$

$$\frac{d\Sigma(q)}{d\Omega} = {}^1N \cdot (\rho - \rho_s)^2 \cdot \langle V^2 \cdot P(q) \rangle \cdot S(q) \qquad\qquad (16)$$

^1N : number density of the aggregates

ρ : scattering length density of the aggregate

ρ_s : scattering length density of the solvent

V : volume of the aggregates

With this modified expression for the structure factor and using eq. 2 to calculate the Rayleigh ratio we were now able to describe the experimental light scattering data very well (see solid line in fig. 8). From this fit procedure we obtained a particle radius of 33.2 Å and a value of - 9.9 for the parameter A. The SANS data were analyzed analogously but here one has to consider that the scattering intensity in neutron scattering is given according to eq. 16 [35]. The scattering length density of the aggregates was calculated to be - 2.48 · 10^{-9} cm^{-2} and that of the solvent (D$_2$O) was 6.36 · 10^{-10} cm^{-2}. An analysis of the SANS with these values data resulted in a fitted curve that is in reasonable agreement with the experimental data (fig. 8). For the particle radius a value of 30.8 Å and for the interaction parameter A one of - 12.9 was obtained. Both these values correspond well with the light scattering results. This detailed analysis of the scattering data by means of the equations for aggregates with an additional attractive interaction potential shows that the size of the aggregates does not change upon the addition of the CL 428. The cross - linking of the aggregates leads to attractions between the aggregates and to an increased scattering intensity at small wave vectors q. The magnitude of the interaction parameter A is just in such a range that it compensates for the repulsiveness of the hard sphere potential. This means that the second virial coefficient of the system is close to zero, which explains why the scattering intensity is much longer linear in the concentration than for the pure TDMAO / decane system where only the repulsive part of the potential is present.

3. 2 Rheological results

In fig. 9 the viscosity of a microemulsion with a total concentration (TDMAO + decane + CL 428) of 16.5 wt % is plotted against the content of the cross - linking agent in the respective system, where again the mass ratio of TDMAO / decane was kept constant at 5.4 : 1. The measurements were performed at three different temperatures, 20, 30, and 40 °C, but the viscosity curves look very similar for all three cases. Only the absolute values decrease with increasing temperature, the convential behavior of viscous solution. Up to 0.75 wt % of CL 428 the addition has only little effect on the viscosity. However a further in-
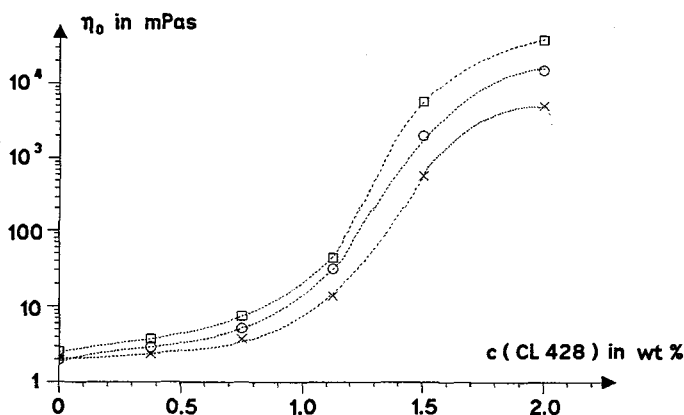
Fig. 9: Zero - shear viscosity η_0 as a function of the CL 428 content at 20 (□), 30 (O) and 40 °C (x) for a total concentration (TDMAO + decane + CL 428) of 16.5 wt %. (m (TDMAO) / m (decane) = 5.4 : 1)

crease to 1.5 wt % changes the viscosity by three orders of magnitude. It is likely that this increase has to be discussed within the framework of percolation theories. Qualitatively it is clear that in our system approximately 2 CL 428 molecules per micelle are required in order to effectively cross - link the system.
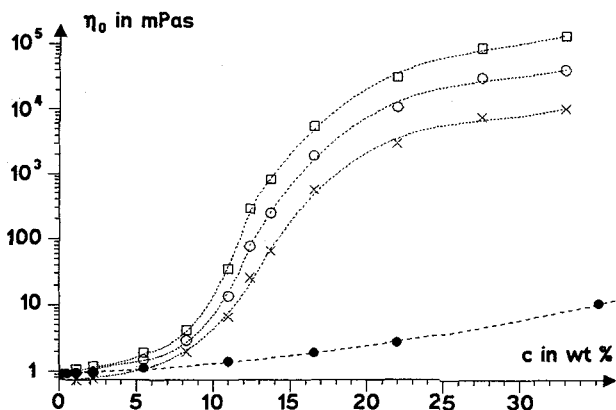

Fig. 10: Viscosity η_0 as a function of the total concentration (surfactant plus decane) at 20 (□), 30 (O) and 40 °C (x). (m (TDMAO) / m (decane) = 5.4 : 1; m (TDMAO + decane) / m (CL 428) = 10 : 1) For comparison the pure TDMAO / decane system : ●.

In the next step of our investigation we studied the rheological behavior of this cross - linked microemul-sion system as a function of the concentration. As in the scattering experiments described above we kept the overall composition constant (m (CL 428) / m (TDMAO + decane) = 1 : 10) and just changed the total concentration of the system. Again the zero - shear viscosity was measured at 20, 30, and 40 °C and is compared in fig. 10 with the viscosity of the corresponding pure TDMAO / decane system (data taken at 25 °C). Obviously the addition of the CL 428 leads to increased viscosity for solutions of more than 5 wt % and in the range of 10 - 15 wt % a marked increase by about 3 - 4 orders of magnitude can be observed. At this concentration an effective cross - linking of the aggregates seems to take place. At still higher concentrations only a comparatively small further increase of the viscosity can be seen and

one seems to approach a limiting plateau value. With rising temperature the steep increase in viscosity is somewhat shifted to higher concentration. At the same time the values of the viscosities become lower by a factor of 3 - 4 for every step of 10 K. The occurence of a plateau value at high concentrations may be explained by the fact that here the interparticle distances are already small enough so that the CL 428 molecules are able to span this distance and anchor their hydrophobic ends in different aggregates, thereby forming a network of interconnected particles.

For the more viscous samples we were also able to measure the shear modulus G_0 at the given three temperatures. Again a strong increase of G_0 can be observed in the range of 10 - 15 wt %. Here it is interesting to note that for the lower concentrations a significant decrease of G_0 with rising temperature can be seen, whereas for the higher concentrations the values are almost independent on the temperature. This may again be explained by the fact that increasing temperature reduces the solvation of the PEO chain in water. Therefore their radius of gyration will decrease which renders the distance smaller that a CL 428 molecule may be able to span between two aggregates. Therefore the intermicellar distance at which effective cross - linking occurs will be reduced with increasing temperature and therefore this point be shifted to higher concentrations. However at concentrations significantly higher than this point no effect will be felt because here the intermicellar distance is anyway smaller than that required for the cross - linking process. Therefore here the number of cross - links will hardly be influenced by the temperature and hence the shear modulus will be little affected. Again we applied the simple model described in 2. 4 to estimate the shear modulus G_0. For this calculation (eq. 11 a) we used the number density [1]N of the CL 428 molecules and the volume fraction Φ of the microemulsion aggregates (ρ (Agg.) = 0.851 g / cm^3 from density measurements). As in the case of the pure thickening compounds good agreement between the theoretical and experimental values can be observed in fig. 11 for the concentrated samples, i. e. above 20 wt %. For the lower concentrations significantly smaller values are observed, which means that here the real density of cross - links is much lower than the one estimated by the simple model, i. e. the probability of having both oleyl chains of the CL 428 in the same aggregate has to be enhanced in comparison to the simple model.
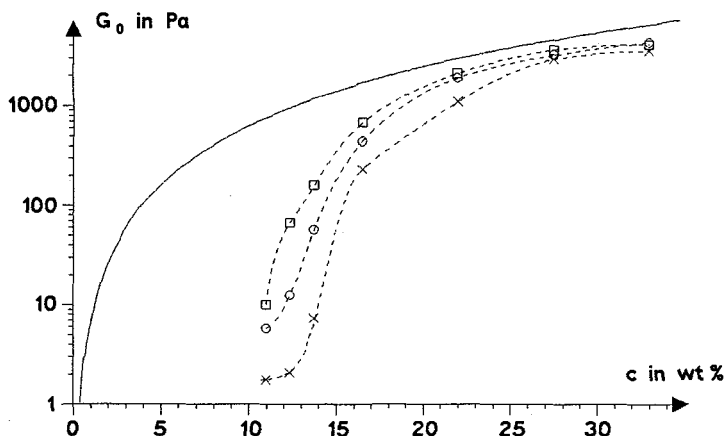

Fig. 11: Shear modulus G_0 as a function of the total concentration (TDMAO + decane + CL 428) at 20 ($\square$), 30 (O) and 40 °C (x). The shear modulus has been estimated according to a simple model (eq. 11 a) plotted as solid line.

Conclusions

In this investigation the aggregation behavior of polyethyleneoxide compounds hydrophobically modified at their their end groups was studied in the binary aqueous system and with addition of O / W microemulsion droplets. Light scattering experiments in the dilute regime (< 5 wt %) showed that in the binary system spherical micellar aggregates with an aggregation number of 20 - 30 are formed. The effective volume fraction of these particles is already increased by a factor of ~ 4 because of the protrusion of the hydrophilic PEO chains into the solution. The viscosity of these solutions stays fairly low for concentrations less than 5 wt %. At higher concentrations a steep increase of viscosity is observed. In the more concentrated samples the amphiphilic polymers are able to bridge the gap between neighboring aggregates. Now the two hydrophobic ends of a molecule may be located in different particles thereby effectively cross - linking these aggregates. The observed shear moduli of these samples are in agreement with a simple network theory.

The O / W microemulsion used for the further investigations contained droplets of a radius of 33 Å. The addition of the cross - linking agent to this microemulsion does not change the size of these droplets as was verified by scattering experiments. However the interactions between these aggregates become modified. In the original microemulsion system the interactions are purely repulsive and can be described by a hard sphere model whereas the addition of the CL 428 leads to an increased attraction between the droplets. Rheological experiments showed that approximately two molecules of the hydrophobically modified PEO compound per aggregate were required in order to effectively cross - link the droplets and increase the viscosity of the solutions by three orders of magnitude. Investigations on a series of constant composition showed that a significant increase of viscosity (by 3 - 4 orders of magnitude) occurs at a total concentration of 10 - 15 wt %. At this concentration the mean distance between the microemulsion aggregates has become small enough for the PEO compound to cross - link the particles. Again the shear modulus of the solutions in the high concentration regime is well described by the simple network model.

Acknowledgement

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