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Interactions in aqueous polypeptide derivative/surfactant systems

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Summary

A new class of compounds of water-soluble polypeptide derivatives have been synthesized and the interactions with the anionic surfactant sodium dodecylsulfate (SDS) studied by rheological and light scattering investigations. The viscosity of the aqueous polypeptide solution passes through a distinct maximum with increasing surfactant concentration. This behaviour, so far only known for hydrophobically modified cellulose derivatives, can be explained by a formation and decay of polymer surfactant networks. The changes caused by microscopic structural parameters through surfactant adsorption are observed by dynamic light scattering and can be correlated with the macroscopic behaviour of the solutions.

Introduction

The adsorption of ionic surfactant molecules at suitable hydrophobic side group polymers causes a considerable increase of viscosity in aqueous solutions (1,2). This behaviour is related to an expansion of the polymer coil and explained by a repulsion of the adsorbed charged surfactant heads of the same kind (3). It has been previously shown (4) that the kind of formation of supermolecular structures strongly depends on the existing secondary structure of the polymer in aqueous solution. A continuous viscosity increase with higher surfactant concentration was observed for flexible polymer coils modified with amphiphilic oligo ethoxy side groups (polyitacones, dextran and amylose derivatives). Comparable cellulose derivatives with similar side groups which exhibit a substantial stiffer polymer backbone reveal a distinct viscosity maximum in aqueous solutions as a function of surfactant concentration. This characteristic viscosity behaviour has been observed for cellulose derivatives only and has been explained by formation and decay of a polymer micelles network of mixed polymer surfactant micelles as physical tie points (1).
In contrast, polypeptides represent still stiffer structures than the cellulosics in solution. Therefore, we undertook an investigation of polyglutamate derivatives with oligo ethoxy side groups to study the interactions with surfactants (SDS) in solution. The amphiphilic character of the oligo ethoxy side group (5,6) leads to good water solubility of the derivatives and offers preferential adsorption sites of the used surfactant SDS (4).
The supermolecular structures formed by the polymer surfactant complexes will be investigated by methods which detect macroscopic changes as the flow behaviour and measured by the viscosity as well as by microscopic structural parameters of the system. These are available by dynamic light scattering experiments and should correlate with the viscosity.

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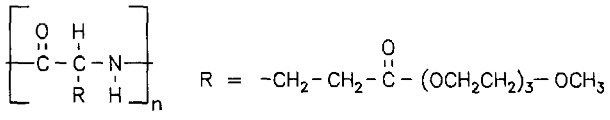
Experimental

The following novel polymer has been synthesized an investigated



$$\left[-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{R}{C}}-\underset{H}{N}-\right]_n \qquad R = -CH_2-CH_2-\overset{O}{\overset{\|}{C}}-(OCH_2CH_2)_3-OCH_3$$

PEO3LG

Synthesis

PEO3LG: 5-Methyl-L-glutamate (MLG; Fluka Chemie AG, Switzerland) 7,1 g was suspended in 100 mL THF and treated with 80 mL of a solution of 20% of phosgene in toluene (Fluka). The suspension was heated to 338 K for 3 h resulting in a clear solution. The formed N-carboxy andydride (MLG-NCA) was precipitated in petroleum ether, washed and dried.

MLG-NCA 3 g was dissolved in 51 mL THF and mixed with 2 mL of a solution of 0,18 mL triethyl amine in 18 mL THF. After 3 days the precipitated poly-γ-methyl glutamate (PMLG1) was filtered off and dried. The higher molar mass compound PMLG2 was obtained with a solution of 20 μL triethyl amine in 53 mL THF treated with 1,45 g MLG-NCA at 263 K. The reaction time lasted 3 days.

PMLG1 and PMLG2 0,5 g, resp., were transesterified with 10 mL triethylene glycol monomethyl ether and 0,5 mL tetraisopropyl titanate (Fluka) in 5 mL diethylene glycol dimethyl ether and the products PEO3LG1 and PEO3LG2 are formed, respectively.

Measurements: Static and dynamic light scattering as well as a combined gelpermeation chromatography/low angle laser light scattering (GPC/LALLS) and viscosity studies were carried out. The principles and the sample preparations have been described in details elsewhere (7).

Results and discussion

The polymers synthesized were identified by IR spectroscopy and characterized with regards to molar mass and its distribution as well as structural parameters (radius of gyration R_g, hydrodynamic radius R_h, second osmotic virial coefficient A_2) by light scattering and GPC/LALLS coupling, respectively. The intrinsic viscosity $[\eta]$, the critical concentration $c^* = [\eta]^{-1}$ (8) were determined by rheological measurements. The molar degree of substitution M.S. was obtained by the method of Morgan (9). The results are collected in table 1.

Special care was applied at all light scattering experiments that the concentrations used for the solutions ranged well below the critical concentration to avoid entanglements and associates which are especially promoted by the oligo ethoxy side groups (10).

The polyglutamate derivatives possess a molar mass distribution comparable with a condensation reaction. An almost complete substitution was obtained with M.S. ≈ 1 for the derivatives considered in contrast to the amylose, dextran and cellulose derivatives (4,10). Besides the cellulose derivatives discussed in an earlier report (4,10), the polyglutamine acid derivatives represent a new class of compounds for which a viscosity maximum is passed by adding SDS in aqueous solutions. The dependence of the zero shear viscosity η_0 on the surfactant concentration [SDS] at 293 K shows figure 1a for the lower molar mass PEO3LG1 and figure 1b for the higher molar mass PEO3LG2. The formation of a viscosity maximum can be detected only from a certain polymer concentration on. The determination

Tab. 1: Characteristic data of the two polymers and their aqueous solutions at 298 K

Polymer Code	PEO3LG1	PEO3LG2
$\langle M_n \rangle /(g \cdot mol^{-1})^{a)}$	110000	190000
$\langle M_w \rangle /(g \cdot mol^{-1})^{a)}$	260000	330000
$\langle M_z \rangle /(g \cdot mol^{-1})^{a)}$	450000	380000
$\langle M_w \rangle / \langle M_n \rangle$	2,4	1,7
$dn/dc/(mL \cdot g^{-1})$	0,166	0,166
$\langle M_w \rangle /(g \cdot mol^{-1})^{b)}$	250000	330000
$A_2/(mL \cdot mol \cdot g^{-2})^{b)}$	$2,3 \cdot 10^{-4}$	$1,9 \cdot 10^{-4}$
$R_g/nm^{b)}$	69,6	81,5
$R_h/nm^{c)}$	34,3	43,7
$[\eta]/(mL \cdot g^{-1})$	63	97
$c^*/(g \cdot mL^{-1})$	$1,6 \cdot 10^{-2}$	$1,0 \cdot 10^{-2}$
M.S.	0,95	0,95

$^{a)}$ GPC/LALLS-coupling $^{b)}$ static light scattering $^{c)}$ dynamic light scattering

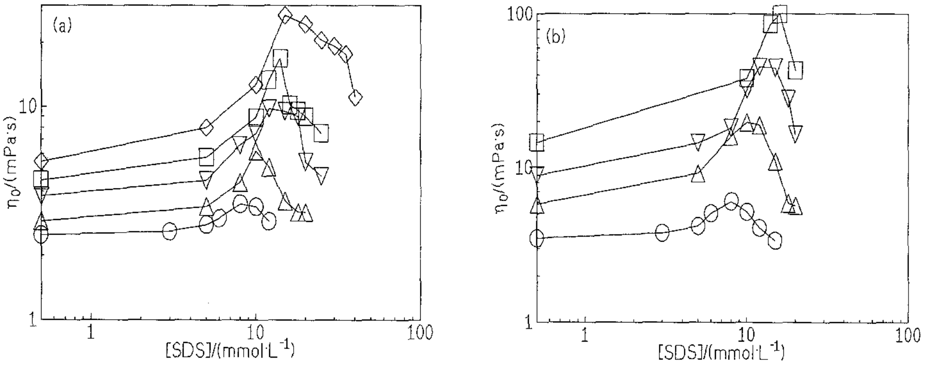


Fig. 1: Dependence of viscosity at zero shear rate η_0 on surfactant concentration [SDS] of aqueous PEO3LG1 (a) and PEO3LG2 (b) solutions at 293 K: $1,0 g \cdot dL^{-1}$ (○), $1,5 g \cdot dL^{-1}$ (Δ), $2,0 g \cdot dL^{-1}$ (∇), $2,5 g \cdot dL^{-1}$ (□), $3,0 g \cdot dL^{-1}$ (◇)

of an effective polymer concentration for which a polymer surfactant network with viscosity maximum is achieved can be determined by a plot of the ratio of maximal obtained viscosity $\eta_{0,max}$ to initial viscosity $\eta_{0,*}$ ([SDS]=0) as a function of the polymer concentration (cf. figure 2). Polymer surfactant interactions are not rheologically detectable below a concentration [PEO3LG] < $0,85 g \cdot dL^{-1}$ for both systems of different molar mass.

The ratio $\eta_{0,max}/\eta_{0,*}$ increases linearly from this effective concentration on. The cellulose derivatives investigated (10) show a similar behaviour.

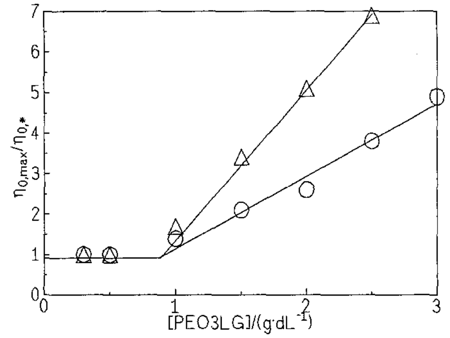


Fig. 2: Ratio of viscosity at viscosity maximum $\eta_{0,max}$ (cf. fig. 1) to viscosity of the same solution without SDS $\eta_{0,*}$ at zero shear rate as a function of polymer concentration [PEO3LG] at 293 K. PEO3LG1/SDS (○) and PEO3LG2/SDS (Δ)

The amount of surfactant necessary to reach the maximum $\eta_{0,max}$ is the same for both systems as clearly revealed in figure 3. However, the higher molar mass compound PEO3LG2 leads to a higher viscosity $\eta_{0,max}$. The linear relationships in the half-logarithmic graphs of figure 3 are expressed by exponential functions $[SDS]=a_1 \cdot \exp(b_1 \cdot [PEO3LG])$ and $\eta_{0,max}=a_2 \cdot \exp(b_2 \cdot [PEO3LG])$. The fitted constants a_i, b_i $(i=1,2)$ and the standard error r are summarized in table 2.

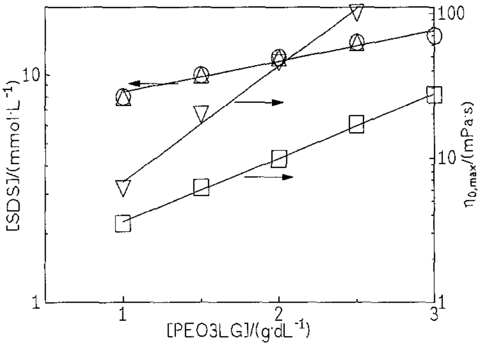


Fig. 3: Viscosity $\eta_{0,max}$ and corresponding surfactant concentration [SDS] as a function of polymer concentration [PEO3LG] at 293 K. PEO3LG1/SDS (○ and □), PEO3LG2/SDS (Δ and ∇)

Tab. 2: Constants a_i, b_i $(i=1,2)$ and standard error r of curves in figure 3 fitted by exponential functions $[SDS]=a_1 \cdot \exp(b_1 \cdot [PEO3LG])$ and $\eta_{0,max}=a_2 \cdot \exp(b_2 \cdot [PEO3LG])$

System	PEO3LG1/	SDS	PEO3LG2/	SDS
Type of curve	[SDS]	$\eta_{0,max}$	[SDS]	$\eta_{0,max}$
$a_i(i=1,2)$	6,08	1,30	6,08	1,07
$b_i(i=1,2)$	0,32	1,02	0,32	1,85
r in %	3	0	3	1

The adsorption of surfactant molecules on the polymer side groups causes, as shown by the flow behaviour, a vicosity increase of the solutions. On the other side the higher viscosity is related to changes in microscopic structural parameters of the dissolved particles e.g. the hydrodynamic radius (7,10). This quantity was investigated by dynamic light scattering at various surfactant concentrations. Angle dependent measurements lead by extrapolation to scattering angle 0 to an apparent diffusion coefficient D_{app} for a specific polymer-surfactant solution of a graph where measured diffusion coefficient versus scattering vector squared q^2 is plotted (10). D_{app} relates to an apparent hydrodynamic radius $R_{h\ app}$ by the Stokes-Einstein equation (11) and may be compared with the zero shear viscosity of the solution considered. A correlation of the microscopic structural parameter of the dissolved particles and the macroscopic behaviour of the aqueous solution follows. The previously investigated amylose (AEO2, AEO3) and dextran derivatives (DEO2, DEO3) with similar or identical side groups as PEO3LG (10) exhibit a linear relationship between $R_{h\ app}$ and η_0. No maximum in the viscosity measurement was obtained (cf. figure 4). The straight lines in figure 4 are expressed by $R_{h\ app}=k_0+k_1\cdot\eta_0$ with specific constants k_0 and k_1 for a specific system (10).

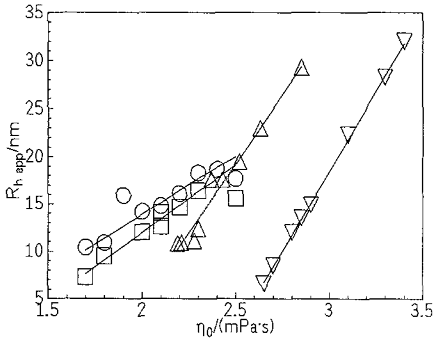


Fig. 4: Correlation between apparent hydrodynamic radius $R_{h\ app}$ and viscosity at zero shear rate η_0 of various dextran (D) and amylose (A)/SDS systems in aqueous solution at 298 K. DEO2: 1,8g·dL^{-1} (Δ), DEO3: 1,0g·dL^{-1} (∇), AEO2: 0,8g·dL^{-1} (○), AEO3: 1,0g·dL^{-1} (□)

In contrast to these as coils in aqueous solution existing derivatives, the increase of the apparent hydrodynamic radius $R_{h\ app}$ with the zero shear viscosity appears no longer linear for the semiflexible or stiff rodlike cellulose and polypeptide derivatives. As representatives for systems with viscosity maxima a cellulose derivative (hydroxyethyl cellulose with diethoxy (EO2) side groups; HECEO2)/SDS and PEO3LG/SDS are represented in figure 5.

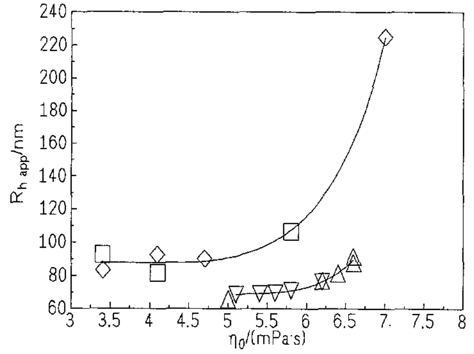


Fig. 5: Correlation between apparent hydrodynamic radius $R_{h\ app}$ and viscosity at zero shear rate η_0 of various polymer-SDS systems in aqueous solution at 298 K. HECEO2: 1,7g·dL^{-1} (Δ and ∇), PEO3LG2: 1,0g·dL^{-1} (◇ and □); Δ and ◇ data points ahead, ∇ and □ after passing the viscosity maximum (cf. fig. 1)

The correlation of $R_{h\ app}$ and η_0 before and after the viscosity maxima has been passed are described by one curve. The graphs of figure 5 support the proposed model of the formation and decay of a mixed polymer surfactant micelle (1,10). The slow increase of $R_{h\ app}$ in the small surfactant concentration range is caused by surfactant adsorption at the side groups and a resulting small expansion of the particles in solution. The extreme increase of $R_{h\ app}$ just ahead of the viscosity maximum reflects the formation of a three dimensional polymer surfactant network. The strong decrease of $R_{h\ app}$ after passing the viscosity maximum points towards a spontaneous decay of the network from the surfactant concentration of the maximum on. In the range of still higher surfactant concentration the surfactant micelles attached to the polymeric side groups will be split off and the viscosity and the hydrodynamic radius decreases further.

The functions decribing this behaviour are represented by $R_{h\ app}=\exp(k'_0+k'_1\cdot\eta_0+k'_2\cdot\eta_0^2+k'_3\cdot\eta_0^3)$ as shown for all the systems investigated including cellulose derivatives (hydroxypropyl cellulose with triethoxy (EO3) side groups; HPCEO3). The best fit parameters k'_i (i=0,1,2,3) and the standard error r describing the calculated curves in figure 5 are summarized in table 3.

Tab. 3: Constants k'_0, k'_1, k'_2, k'_3 and standard error r of curves in figure 5 and HPCEO3/SDS fitted by the function $R_{happ}=\exp(k'_0+k'_1\cdot\eta_0+k'_2\cdot\eta_0^2+k'_3\cdot\eta_0^3)$

System	HECEO2/SDS	HPCEO3/SDS	PEO3LG2/SDS
k'_0	-5,95	16,0	2,44
k'_1	5,96	-19,63	1,56
k'_2	-1,17	10,92	-0,40
k'_3	0,076	-1,84	0,034
r in %	2	0	1

Conclusions

The polyglutamine acid derivatives represent systems which like the cellulose derivatives form polymer micelle networks when surfactants are added to the aqueous solutions. The tie points of the network are represented by mixed polymer surfactant micelles.

The adsorption of the surfactant at the polymeric side groups causes an increase of the hydrodynamic radius. This microscopic structural quantity can be correlated functionally to the zero shear viscosity which represents a macroscopic quantity.

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