Solution Viscosity of Polyelectrolyte–Surfactant Complexes: Polyelectrolyte Behavior in Nonaqueous Solvents

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ABSTRACT: Polyelectrolyte–surfactant complexes made of poly(styrenesulfonate) and various cationic surfactants are "synthesized" by common precipitation in water. Redissolved in polar organic solvents, these complexes show polyelectrolyte behavior. This behavior is quantitatively described with a modified Hess–Klein equation where the fitting parameters have the meaning of a hydrodynamic size, an effective charge density, and a salt concentration. The influence of complex hydrophobicity, the polarity of the solvent, and the role of small amounts of water are discussed by means of the experimentally determined Hess–Klein parameters. Dynamic light scattering in dilute solutions reveals a complex relaxation typical for coupled or strongly interacting systems.

1. Introduction

Polyelectrolyte–surfactant (PE–Surf) complexes form spontaneously and in a highly cooperative manner when aqueous solutions of polyelectrolytes and oppositely charged surfactants are mixed (see, for instance, refs 1–5). These complexes are well-defined with respect to their stoichiometry and are highly stable. Recently, we have shown that these PE–Surf complexes not only exhibit a well-ordered solid-state structure but also can be redissolved in polar organic solvents and show some unconventional and interesting solution properties.[6] It was speculated that these observations might be explained by assumption of a polyelectrolyte behavior in these systems.

Also, in 1994, MacKnight et al. published on the viscosity behavior of ionomer-like, nonstoichiometric PE–Surfs made of poly(*N*-ethyl-4-vinylpyridinium bromide) and sodium dodecyl sulfate.[7] Their data in chloroform, however, show a standard behavior with low intrinsic viscosities and a coil contraction with increasing charge densities.

The aim of the present paper is to resolve this apparent contradiction by a more extensive characterization of the viscosity behavior of these complexes. For this purpose, the hydrophobicity of the complexes as well as the solvent polarity is varied. In addition, we examine the influence of small amounts of water on the solution viscosity which also depends on complex hydrophobicity.

Since PE–Surf complexes dissolve in a wider variety of solvents (compared to standard polyelectrolytes), viscometric examinations of these materials also can contribute to a better understanding of the physical behavior of charged polymers in general, as shown by the quantitative fulfillment of a modified Hess–Klein description of the solution viscosity.

2. Experimental Section

2.1. Polymer Synthesis. Sodium poly(styrenesulfonate), PSS, is made by sulfonation of anionically polymerized polystyrene (M_w = 449 000, M_w/M_n < 1.05) with H_2SO_4/P_2O_5 following the Vink procedure.[8] The PSS is dialyzed and used as a 1% solution in water.

Complexation and purification of the complexes are performed as described in our earlier publication.[6] Dodecyltrimethylammonium bromide (C_{12}), tetradecyltrimethylammonium bromide (C_{14}), hexadecyltrimethylammonium bromide (C_{16}), and trioctylmethylammonium bromide ($C_8{}^3$), all from Aldrich Chemical Co., are used as surfactants. The 1:1 stoichiometry and the absence of low molecular weight salts and additional free surfactant molecules are checked for all complexes with elemental analysis; the relative amounts of Na^+ and Br^- are usually below 0.01%. The complexes are named by combination of the polymer abbreviation and the length of the surfactant chain; e.g., PSS–C_{16} names the complex of poly(styrenesulfonate) and hexadecyltrimethylammonium counterions.

2.2. Viscometric Measurements. All viscosity measurements are performed at 25.0 °C using an automatic Schott AVS360 instrument (Ubbelohde viscometers), which allows reproduction of the flow times with an accuracy of 0.03 s. The solutions are made by dissolving the samples in freshly distilled solvents dried with molecular sieve or sodium, respectively. The flow times are taken by measuring subsequent dilutions of a stock solution of 10 g/L, and each flow time is reproduced five times. The dilution and measurements are stopped when the viscosity difference of the complex solution and pure solvent drops below 10%.

The shear rate dependence of the viscosity which is well-known for latex particles[9] or linear polyelectrolytes[10] in salt-free aqueous solution is simply neglected. It is assumed that the present measurements are already very close to the zero shear limit. The repetitions of some experiments with capillaries of different size essentially reproduce the presented results.

2.3. Dynamic Light Scattering. Light scattering experiments are carried out in ethanol and DMF at 20.0 °C. A commercial spectrometer from ALV/Langen, consisting of an ALV ISP86 goniometer and an ALV5000 multi-τ correlator is used. The measurements are performed using the 532.8-nm line of a cw frequency-doubled, diode-pumped Nd-YAG laser (ADLAS 425c) with 300-mW output power. The complex solutions are filtered through 0.45-μm Millipore filters.

3. Results and Discussion

Depending on the hydrophobicity of the polymer backbone and the length and number of the surfactant

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tails, the complexes dissolve in a number of alcohols, amidic solvents, or chloroform. Our experiments demonstrate that the reduced specific viscosity, η_{sp}/c_P, increases strongly with decreasing concentration, a fact which is well-known for polyelectrolytes. Classically, the apparent divergence of the reduced specific viscosity at small polymer concentrations c_P is linearized[11] with a so-called Fuoss–Strauss plot based upon the empirical equation (1):

$$\eta_{sp}/c_P = (A + Bc_P^{0.5})^{-1} \tag{1}$$

This equation, introduced by Fuoss and Strauss in the 1940's,[12–14] linearizes polyelectrolyte data quite well. In the more recent polyelectrolyte literature, some theoretical explanations for the meaning of A and B are given. Witten and Pincus, for instance, found within the framework of their theory[15] that $A \sim Zd^3$, where d is the distance between two successive charges and Z the number of charges on each chain. An alternative approach toward the Fouss–Strauss behavior was proposed by Rabin,[16] who showed that in his theory the ratio $A/B \sim Z$. However, some of the assumptions which have been made to obtain the simplicity of the Fuoss–Strauss law are at least questionable.[17]

More recent and more precise experiments show that the intrinsic viscosity curves do not diverge but show a pronounced maximum at very low concentrations.[18–27] This makes a Fuoss–Strauss-type extrapolation meaningless. It is possible to describe this behavior with the Rabin theory, but some artificial-looking assumptions have to be made as well.[22]

For the present set of experiments, it is advantageous to return to the more basic Hess–Klein approach.[28] On the basis of the weak coupling approximation (WCA), they derived relaxation equations for solutions of charged hard spheres in the presence of salt. For the excess viscosity ($\eta - \eta_0$) due to electrostatic interactions, the WCA predicts:

$$\eta - \eta_0 = \frac{1}{960\pi}\zeta_0\left(\frac{4\pi e^2}{\epsilon\epsilon_0 kT}\right)^{1/2}\frac{Z_{\mathrm{eff}}^{\,4}c_P^{\,2}}{(\Sigma Z_i c_i)^{3/2}} \tag{2}$$

Here, η_0 is the viscosity of the solvent, ζ_0 the hydrodynamic friction coefficient of the charged particle, Z_{eff} the effective number of charges e of a particle, and Z_ic_i all the charge carriers being present in solution with the concentration c_i and a charge number Z_i. Recently, Antonietti and Förster pointed out that this formula is conveniently transformed to eq 3 which can be used for fitting the reduced specific viscosity of polyelectrolytes with molecular parameters only.[29] In the limit of monovalent ions, we obtain:

$$\frac{\eta_{sp}}{c_P} = \frac{1}{160}r_H\left(\frac{4\pi e^2 N_L}{M_P\epsilon\epsilon_0 kT}\right)^{1/2}\frac{Z_{\mathrm{eff}}^{\,4}c_P}{\left(2\frac{M_P}{M_S}c_S + Z_{\mathrm{eff}}c_P\right)^{3/2}} \tag{3}$$

Here, M_S and M_P are the molecular weights of the salt and polymer, respectively. The concentration in eq 3 is now in grams per liter, the typical dimension of the viscosity experiments. This equation exhibits a maximum at $(\eta_{sp}/c_P)_{max} = 4M_Pc_S/M_SZ$ and has a high-c_P asymptote of $\eta_{sp}/c_P \sim r_HZ_{\mathrm{eff}}^{5/2}c_P^{-1/2}$. The maximum results from a competition between screening of electrostatic interactions that scale as $c_P^{-1/2}$ and decreasing intermolecular distances scaling as $c_P^{-1/3}$. At the $(\eta_{sp}/c_P)_{max}$ the pair potential has its maximum; it decreases upon dilution because of an increase of intermolecular distances and also decreases with increasing concentration due to screening of electrostatic interactions.

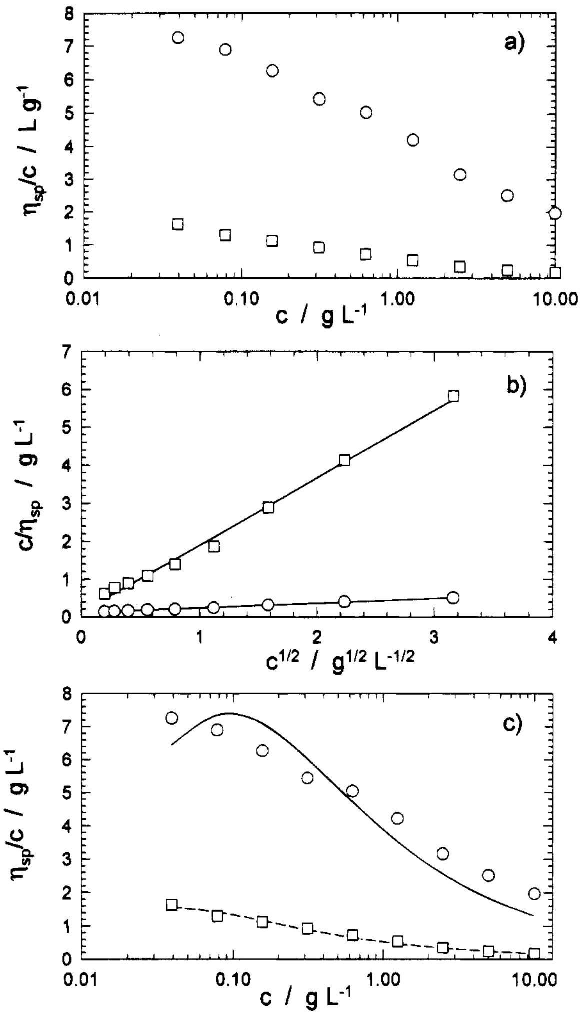

Figure 1. Comparison of the concentration dependence of the intrinsic viscosity of PSS–Na (○) in water and PSS–C_{16} in DMF (□). The data are presented in a standard plot (a) as well as a Fouss–Strauss presentation (b) or are fitted according to Hess–Klein (c). The fit parameters are given in Table 1 and Figure 3.

The hydrodynamic radius of the polymer r_H, Z_{eff}, and the low molecular weight salt concentration c_S are used as fitting parameters. c_S is in the present case given by ionic, low molecular weight impurities.

For illustration, Figure 1a shows the viscosity effects of a PE–Surf (PSS–C_{16}) in DMF, an organic solvent, and the parental polyelectrolyte (sodium poly(styrenesulfonate)) in water. In both solvents we observe polyelectrolyte behavior, i.e., a sharp increase of the intrinsic viscosity with decreasing concentration. The values of the complex in DMF clearly exceed standard values of uncharged polymers with the same degree of polymerization by far but are a factor of 4 smaller than the similar polyelectrolyte counterpart in pure water. A description of the Fouss–Strauss linearization is presented in Figure 1b. The PE–Surf data are also well fitted to the modified Hess–Klein equation, as seen in Figure 1c. The fit to the polyelectrolyte exhibits a systematic upward deviation of η_{sp}/c_P. This has also been observed by Cohen et al. in the case of high molecular weight polyelectrolytes.[22] The reason for this

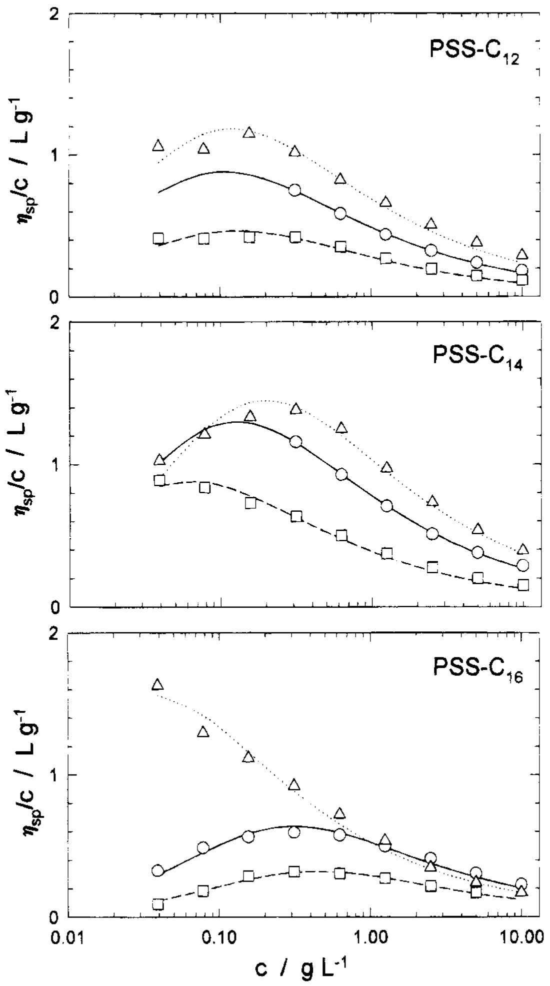

Figure 2. Solvent dependence of the viscosity/concentration curves for the three complexes PSS$-C_{12}$, PSS$-C_{14}$, and PSS$-C_{16}$: (△) DMF; (○) ethanol; (□) isopropyl alcohol. The lines are fitted according to eq 3 and the parameters given in Table 1.

Table 1. Fit Parameters According to Equation 3 for Different Solvent/Complex Combinations

sample	solvent	r_H/nm	Z_{eff}	$c_S/10^{-5}$ g/L
PSS$-C_{12}$	ethanol	72.40	8.90	2.72
	propanol	51.20	7.70	2.86
	DMF	102.00	9.70	3.32
PSS$-C_{14}$	ethanol	94.60	9.80	3.34
	propanol	59.80	8.21	1.37
	DMF	134.00	10.60	5.62
PSS$-C_{16}$	ethanol	92.10	9.00	7.09
	propanol	67.70	7.80	8.75
	DMF	84.80	9.30	0.83

deviation is still unclear. The superior description with the Hess–Klein theory becomes apparent, if the viscosity exhibits a peak, which cannot be linearized by the empirical Fuoss–Strauss equation. This is demonstrated in Figure 2a–c which presents the solution viscosity of PSS$-C_{12}$ (a), PSS$-C_{14}$ (b), and PSS$-C_{16}$ (c) in the three organic solvents in isopropyl alcohol, ethanol, and DMF. These solvents are chosen for their different dielectric constants ($\epsilon = 36.7$ for DMF, $\epsilon = 24.3$ for ethanol, $\epsilon = 18.3$ for isopropyl alcohol). At a first glance, it is observed that the viscosity simply follows the solvent polarity: the values in DMF exceed the corresponding ones in ethanol which are larger than the isopropyl alcohol values.

Table 1 shows for a more quantitative discussion the numerical values of the fit parameters of the experimental data seen in Figure 2a–c. The relative error of Z is about 10% and is only slightly larger for r_H.

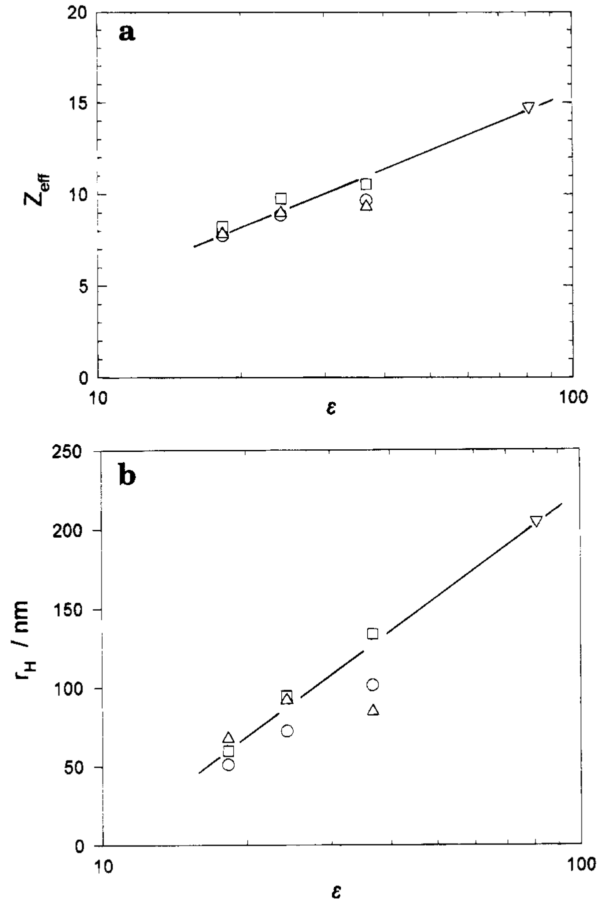

Figure 3. Dependence of the effective charge number per polymer Z_{eff} (a) and of the hydrodynamic radius r_H (b) on the dielectric constant of the solvent, as taken from the fits of eq 3: (○) PSS$-C_{12}$; (□) PSS$-C_{14}$; (△) PSS$-C_{16}$.

We obtain values for r_H in the region of 50 nm (isopropyl alcohol) to 130 nm (DMF), which is at least physically meaningful, and for a degree of polymerization of 4300 in the right order of magnitude. The fitted effective number of charges per particle is quite low and lies constantly between 7 and 10. It is difficult to relate the effective charge Z_{eff} to the number of charges Z on the chain. Taking the approximation by Rabin, $Z \sim Z_{eff}^2$ (from ref 22), we obtain 50–100 charges/chain. It must be underlined, however, that organic solvents usually do not promote the dissociation of ions. Within this restriction, a relative dissociation of 1 charge per 40 monomer units is also in a reasonable range. The fitted concentration of impurities c_S again is very low (10^{-5}–10^{-6} mol/L) and might result from ionic impurities in the solution, although considerable care was taken to prepare "salt-free" solutions. This reflects the enormous sensitivity of the described behavior against low molecular weight salt.

Parts a and b of Figure 3 present the dependence of the fitted hydrodynamic size r_H and effective charge number Z_{eff} on the dielectric constant of the solvent, ϵ. For comparison, we also include the values fitted for PSS–Na in water, as shown in Figure 1. Out of the experimental error, the size as well as the charge number increases with increasing solvent polarity, which might be expected too. Since eq 3 already corrects for the increased field strength in more unpolar solvents (by dividing by ϵ), the influence by an improved polyelectrolyte character in more polar solvents is detected only. The increase, however, is less than expected, for instance, by the Manning theory,[30] and theoretical assistance for a better description of Figure 3a,b is surely needed.

For a more practical point of view such as the optimization of the polyelectrolyte effects by the choice of an appropriate counterion, it is also meaningful to present the data in another context. Parts a and b of Figure 4 show the counterion dependence of the solution viscosity by comparing the data of the complete series of complexes PSS–C_{12} to PSS–$C_8{}^3$ in DMF (a) as well as in ethanol (b). The highest intrinsic viscosities in both solvents are obtained for the C_{14} derivative, as already seen by the highest Z_{eff} values in Table 1. Apparently, C_{14} complies best with the somewhat opposite requirements of counterion solubility and hydrophobic complex/surfactant interaction. The other complexes behave, within experimental errors and in spite of the varying amounts of impurities, the fitted c_S, quite similarly. Just in the case of PSS–$C_8{}^3$ in ethanol, the curve has a somewhat different shape and cannot be described according to Hess–Klein alone.

It was Kaji who pointed out[31,32] that in the limit of weaker interactions the influence of polymer conformation and the influence of electrostatic interactions on the intrinsic viscosity of linear polyelectrolytes may be simply additive. A similar approach is also commonly used for the description of the rheology of colloidal dispersions where the influence of near-field hydrodynamics, interparticle forces, and Brownian motion on the viscosity is taken as additive.[33] Therefore, we may incorporate eq 2 in the familiar expression for the intrinsic viscosity of polymer solutions in the following way:

$$\frac{\eta_{sp}}{c_P} = [\eta]\left[1 + k_h[\eta]c_P + \left(\frac{\eta_{sp}}{c_P}\right)_{HK}\right] \qquad (4)$$

where $[\eta]$ is the intrinsic viscosity, k_h is the Huggins coefficient, and the term $(\eta_{sp}/c_P)_{HK}$ represents the expression in eq 3. It must be underlined that such a treatment makes use of the crude assumption that the degree of dissociation does not change with the polymer conformation which again might be concentration dependent. Nevertheless, the Kaji approach is helpful to describe the viscosity complexes in solvents where the electrostatic interactions lead to effects in the order of the intrinsic viscosity of the hypothetically uncharged chain. This is particularly helpful for the most hydrophobic complex, PSS–$C_8{}^3$, the data of which are presented in Figure 5.

This complex also dissolves in less polar solvents such as acetone (ϵ = 20.7), tetrahydrofuran (ϵ = 7.39), chloroform (ϵ = 4.81), or toluene (ϵ = 2.38). Due to the widespread data, a logarithmic presentation was chosen. Obviously, we can observe complete transition from polyelectrolyte behavior to one of an uncharged polymer by simple solvent variation.

The toluene solutions are stable but already exhibit some opacity, whereas all other solutions look molecularly dissolved. For this reason it is also questionable whether the value of the intrinsic viscosity of $[\eta]$ = 40 cm^3/g (the intercept with the y-axis) really reflects a molecular property. The viscosity behavior of PSS–$C_8{}^3$ in chloroform and THF is only slightly perturbed by ionic interactions and allows extrapolation to vanishing concentrations; the $[\eta]$ values of 65–80 cm^3/g are still too small for a linear polymer of comparable molecular weight and can be related to a swollen, but compact, conformation where the ionic structures get intramolecularly clustered inside each polymer molecule. A similar observation was already made by McKnight and Kabanov, as stated above.[7]

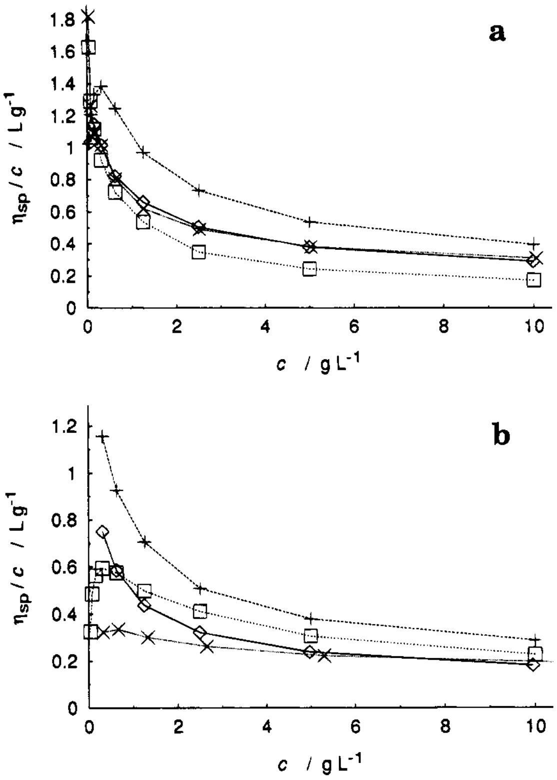

Figure 4. Counterion dependence of the viscosity/concentration curves in DMF (a) as well as in ethanol (b). (◇) PSS–C_{12}; (+) PSS–C_{14}; (□) PSS–C_{16}; (×) PSS–$C_8{}^3$.

In acetone, isopropyl alcohol, and ethanol, more or less polyelectrolyte effects are observed, and the curves can be described by a combination of molecular hydrodynamics and intermolecular interaction only. A quantitative fit according to eq 4 can describe this behavior, as seen by the lines along the data points in Figure 5. Due to the large number of parameters, however, it is impossible for the present data set to extract quantitative information, since each parameter value is rather unstable.

It might be speculated that, during all measurements described above, a spurious amount of water can play a crucial role since dissociation processes are strongly influenced by hydration. To exclude this argument, we have repeated in a last set of experiments the measurements of two complexes with different hydrophobicity, PSS–C_{16} and PSS–$C_8{}^3$, in ethanol and have added 5% water. These data are shown in Figure 6. Only a slight increase due to simple dissociation is observed for PSS–C_{16}, whereas even a decrease due to a decreased solvent quality is detected for PSS–$C_8{}^3$. These are clear indications that the dissociation takes place already in the pure solvents and that a special function of water can be excluded.

At the end, we wish to show that the polyelectrolyte behavior of PE–Surf is not only seen in viscosity experiments but is also present in the relaxation behavior, as detected by dynamic light scattering.

Figure 7a shows typical relaxation curves, obtained for a 1 g/L solution of PSS–C_{16} in DMF at three different scattering angles. With respect to Figure 2, this concentration is clearly above the critical concen-

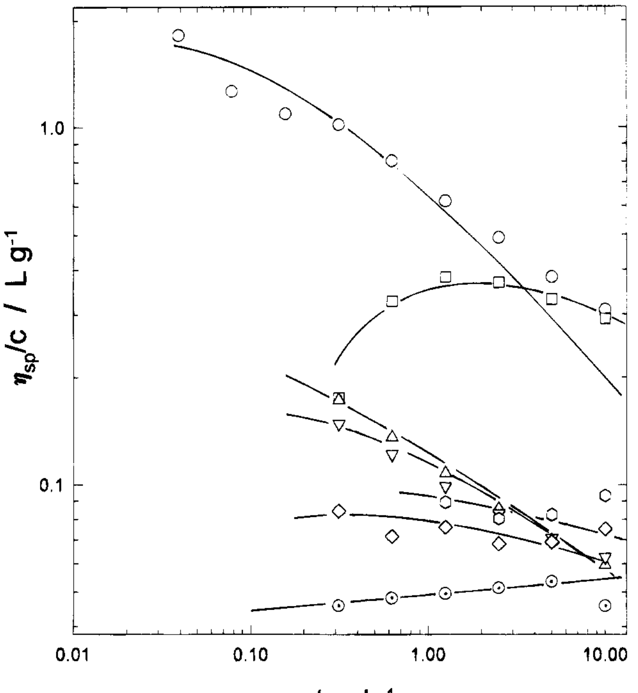

Figure 5. Viscosity/concentration curves for PSS–$C_8{}^3$ in seven different solvents covering a wide range of polarities: (○) DMF; (□) methanol; (▽) isopropyl alcohol; (△) acetone; (O) chloroform; (◇) THF; (⊙) toluene. The lines indicate a fit according to Kaji.

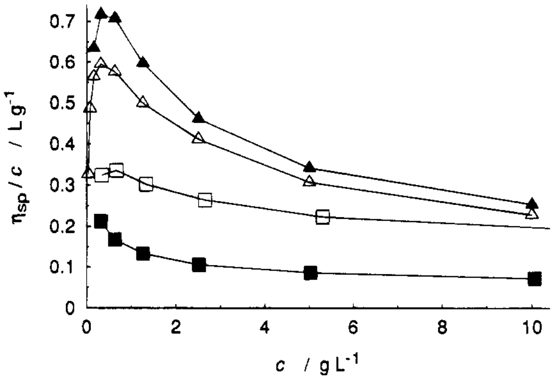

Figure 6. Influence of residual amounts of water on the viscosity/concentration curves of PSS–C_{16} (△,▲) and PSS–$C_8{}^3$ (□,■). Open symbols: dry ethanol. Filled symbols: ethanol + 5 wt % H_2O.

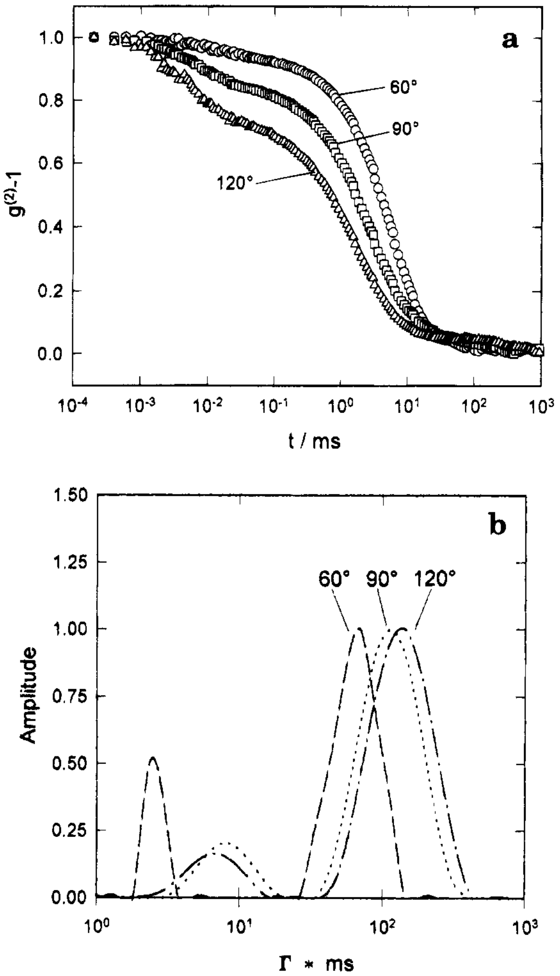

Figure 7. Normalized relaxation curves (a) and corresponding distribution of relaxation times (b) of PSS–C_{16} at 1 g/L in DMF, as determined by light scattering. The data of three different scattering angles (60°, 90°, 120°) are superimposed to demonstrate the diffusive nature of both modes.

tration of the maximum of the intrinsic viscosity, or, in other words, in the interacting regime. A bimodal relaxation with two diffusive processes is obtained which is well-known for the behavior of polyelectrolytes in aqueous, salt-free solutions.[34,35] The corresponding bimodal distribution of relaxation times as obtained from the inverse Laplace transformation of the relaxation functions is shown in Figure 7b. The fast mode is usually attributed to Nernst–Hartley diffusion, whereas the nature of the slow mode is still unknown.[17]

The presence of these interactions also prohibits a characterization of molecular quantities by static and dynamic light scattering, which would be helpful for judging the meaning of the fitted r_H values.

4. Conclusion and Outlook

We have shown that PE–surfactant complexes exhibit polyelectrolyte behavior in polar organic solvents, the magnitude of which depends on the surfactant counterion and solvent. The viscosity curves are quantitatively described with a modified Hess–Klein approach, thus resulting in an effective number of charges Z_{eff}, a hydrodynamic radius r_H, and a concentration of ionic impurities c_S only. All of these fitted quantities have a magnitude which is physically meaningful and depend systematically on the dielectric constant of the solvents.

For the most hydrophobic complex of the series, it was possible to take unpolar solvents, thus resulting in a ionomer-like viscosity curve. In this case, one can observe the complete transition from polyelectrolyte to standard behavior by simple solvent variation.

The simplicity of PE–surfactant complexes as model systems will allow some experiments which will be interesting for a better understanding of the physical behavior of polyelectrolytes in general. With our modified Hess–Klein approach we can determine, for instance, the dependence of the effective charge number Z_{eff} on the molecular weight and on the molecular topology (e.g., linear chains versus spheres). This will allow a better understanding of colloidal interactions in such nonaqueous systems. In a second step, it might be possible to return to the more complicated, but also more important, case of water as a solvent. The description by Hess and Klein is here, as seen in Figure 1, much less convincing, which should be due to structural changes like chain extension and an increased ion activity of the polyelectrolytes at low concentrations.

This must be considered by some modifications on the basic Hess–Klein equation.

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