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Scaling Properties of the Shear Modulus of Polyelectrolyte Complex Coacervates: A time-pH Superposition Principle

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M. Tekaat^a, D. Bütergerds^a, M. Schönhoff^a, A. Fery^b, C. Cramer^{*a}

We analyze the scaling properties of pH-dependent shear modulus spectra of complex coacervates made of weak polyanions and strong polycations. For the first time, we report on a “time-pH superposition principle”. This principle implies that the charge density in complex coacervates made of not fully charged polyions only influences the time-scale of the relaxation dynamics, but not the mechanisms of the underlying dynamics.

Scaling relations based on superposition principles are an important tool for analyzing frequency-dependent quantities. They allow predicting physical properties of materials beyond the experimental ranges the materials have been studied in. Typical physical quantities which are known to follow superposition principles are, for example, the electrical conductivity and permittivity, and the shear modulus. The most well-known of these scaling procedures is the *time-temperature superposition principle* (TTSP)^{1,2}, application of which can be found for all of the above mentioned physical quantities. It implies that frequency-dependent spectra of the investigated physical quantity determined at different temperatures, T , can be scaled onto a common master curve, if the respective quantity and the frequency scales are properly normalized. In other words, the shape of the spectra is independent of temperature; thus T -dependent spectra are just shifted with respect to each other. The physical principle behind this feature is that variation of temperature only changes the rate of the underlying dynamics (which is then probed on different timescales) without changing the mechanism itself. The time-temperature superposition principle is applicable for a variety of materials such as semiconductors³, inorganic crystals⁴ and glasses⁵, ionic liquids⁶ and polymeric systems^{7,8}, when a suitable temperature range is chosen. In this work we focus on polyelectrolyte complex coacervates. Polyelectrolyte complexes are materials resulting from electrostatic interactions between highly charged polycations and poly-

anions. Apart from the “intrinsic” charge compensation of opposite charges on the polyions, additional small ions like alkali or halide ions might also be incorporated as “extrinsic” charge compensators between the polyelectrolyte chains. In ref. [7] it was shown for the first time that the conductivity spectra of different types of dried polyelectrolyte complexes (PEC) follow the time-temperature superposition principle which led to new conclusions about the changes of the number density and the mobility of small ions present in different types of PEC.

In recent years, other superposition principles have been reported. In ref. [9] it was shown that the relative humidity (RH) of the environment of PEC has a similar influence on the ionic conductivity spectra as temperature has. The reason is that the absorption of water molecules into the solid PEC lowers the activation enthalpy for the ion transport process. The validity of a *time-humidity superposition principle* (THSP) for RH-dependent conductivity spectra therefore implies that this lowering of the activation barriers does not only influence the long-range transport probed by the dc conductivity, but also the ion dynamics occurring on shorter time and length scales. The latter dynamics is probed in the dispersive part of the conductivity spectra⁹.

Combination of polyelectrolyte anions and cations cannot only lead to the formation of PEC precipitates which are subject of the above cited studies. Below a critical salt concentration, the formation of two liquid phases—a water-like and a viscous phase—may occur, if solutions of polycations and polyanions are mixed with each other. The water-like phase typically contains only very few polyions, whereas the viscous phase, termed coacervate phase, contains the strongly swollen PEC.

Recently, Spruijt et al.^{10,11} reported on an extensive scaling study of the frequency-dependent mechanical properties of coacervates made of poly(acrylic acid) (PAA) polyanions and of poly(N,N-dimethylaminoethylmethacrylate) (PDMAEMA) polycations. They found a new scaling principle for the shear modulus, termed *time-salt superposition principle*. They proved that the content of the added salt influences the relaxation times of the modulus spectra (both

^a Institute of Physical Chemistry, University of Muenster, Corrensstraße 28/30, 48149 Münster, Germany

^b Department of Physical Chemistry II, University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany

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real and imaginary parts) significantly and acts as a scaling factor for the complex shear modulus. Also the absolute values of the shear moduli are influenced by the salt content, but the variation is only small as compared to the variation of the relaxation times and can be attributed to density changes^{10,11}. Spruijt et al. used fixed pH-values at which both, polyanions and polycations, are almost fully charged. In their investigated stoichiometric complexes, the average distance between the charged groups on either type of polymers was therefore always constant.

In our study presented here, we changed the effective charge density (given by the degree of dissociation) on the weak polyanions by varying the pH-values. The 1:1 ratio of negative to positive charges in the coacervates was always kept constant. We will show for the first time that the frequency-dependent complex shear modulus of PEC coacervates prepared from polyions with a varying degree of dissociation, obeys scaling relations. We modified both, pH-value and salt content. We will show that both modifications, either additional salt (here KCl) or the degree of dissociation of the polyions influence the dynamics of the binding processes and how these different influences can be separated from each other. We conclude that the charge density of the polyanions has a significant effect on the complex dynamics and that this influence is the stronger the higher the salt content is. We investigated a series of complex coacervates made of cationic poly(diallyldimethyl ammonium chloride) (PDADMAC, $M_w = (100,000 \text{ to } 200,000) \text{ g/mol}$, 20 %wt. in H_2O) and of anionic poly(acrylic acid) (PAA, $M_w = 100,000 \text{ g/mol}$, 35 %wt. in H_2O) prepared at different salt concentrations and different pH-values. The water was ultrapure with a resistance of more than $18.2 \text{ M}\Omega/\text{cm}$. For polyelectrolyte complex formation stock solutions of the two polyelectrolytes (1.76 M for PAA and 0.88 M for PDADMAC) were made. The overall concentration of PAA in the PEC was fixed as 0.11 M for all batches (40 mL). Since PAA is a weak polyelectrolyte, first the degree of dissociation of PAA in solution at different salt concentrations was determined from titration curves (potentiostatic titration with 1 M KOH) to calculate the appropriate volume of PDADMAC solution to be added, see Fig. 1. Addition of KCl resulted in a large shift of the titration curve. However, the difference between curves determined for solutions with 0.25 M KCl and with 0.50 M KCl, respectively, was very small. Replacement of K^+ by Na^+ had a negligible effect. Comparison with published data shows that our titration curve of the PAA solution without added KCl is in good agreement with data obtained by Bromberg^{12,13} and Philippova et al.^{12,14} The ratio of the positively and negatively charged groups on the respective polyions was always 1:1. For the coacervates with a 0.25 M and 0.50 M KCl concentration, the corresponding amount of KCl was added to both PAA and PDADMAC stock solutions. To adjust the pH, potassium hydrochloride or hydrochloric acid (both 1 mol/L) were added to both stock solutions, respectively, before the complexation process was started. Mixing was done from two solutions of identical pH, followed by shaking intensively for a few minutes. Upon mixing in a certain pH-range, complexation occurs if the salt concentration is not too high. The formed PEC appears either as a gel-like substance in the case of a coacervate or as a white solid in the case of a precipitate formation. Phase separation occurs after several hours

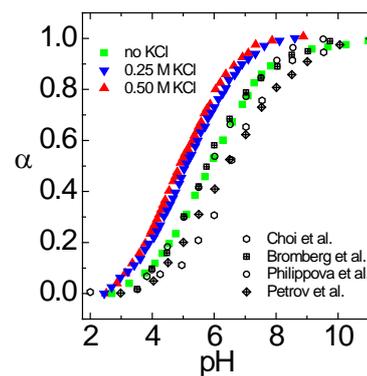


Fig. 1 Degree of dissociation of PAA solutions with different amounts of KCl (full symbols (this work), open symbols (literature data)). The literature data were determined for PAA solutions without additional KCl and have been redrawn from Fig. 2 in ref. (12). Original data are published in refs. (12)-(15).

and after two days the samples were centrifuged at 1000 g for 15 minutes and then left for three days for equilibration.

Measurements of the pH-value in the coacervate phase showed that the pH-value is the same as in both polyion stock solutions. This implies that under the chosen conditions changes in the degree of dissociation of PAA upon complexation are negligible.

Frequency-dependent spectra of the complex shear modulus $G^*(\omega)$ were determined in the oscillation mode with a rheometer Physica MCR101 by Anton Paar using a truncated cone (CP50-0.3 or CP25-1)/plate configuration. Data were taken at ambient temperature (25 °C).

Fig. 2 (a) is a double-logarithmic plot with spectra of the real part G' and of the imaginary part G'' of the complex shear modulus, respectively, as a function of the angular frequency, ω , at various pH-values. The measured data are typical of a viscoelastic material, for which G' is a measure for the stored energy, whereas G'' reflects the energy dissipated during the shearing process. The fact that at a fixed angular frequency the loss modulus G'' is larger than the storage modulus G' , indicates that the complex coacervates behave rather like viscoelastic fluids than like viscoelastic solids. With increasing ω , however, the difference $\Delta G = G'' - G'$ decreases. A transition point is expected at frequencies above our experimentally accessible frequency window. This trend is best seen at pH = 5. The decrease of ΔG with ω implies that on short time scales (corresponding to large angular frequencies), the material behaves more and more like a viscoelastic solid.

Fig. 2 (a) indicates that the pH-value shifts the G'' and G' spectra on the frequency scale. The question whether the spectra are just shifted or whether there is an additional change of the spectral shape can be tested by a scaling analysis in which $\log_{10}((\omega/s^{-1}) \cdot f_{\omega,pH})$ is used instead of $\log_{10}(\omega/s^{-1})$. All spectra were scaled by introducing suitable scaling factors $f_{\omega,pH}$ to match the spectra taken at pH = 8.

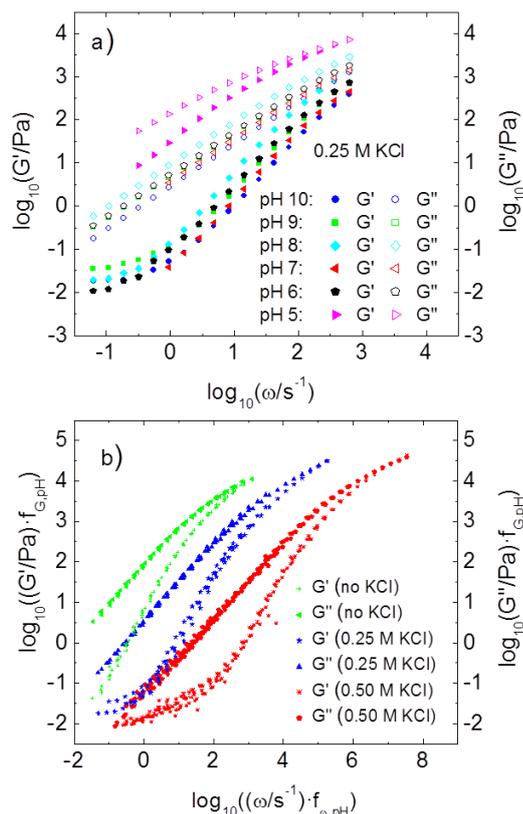


Fig. 2 (a) pH-dependent spectra of the real part $G'(\omega)$ (full symbols) and of the imaginary part $G''(\omega)$ (open symbols) of the complex shear modulus $G^*(\omega)$ for PAA/PDADMAC complex coacervates prepared at a salt concentration of 0.5 mol/L. (b) Master curves resulting from scaling of individual shear modulus spectra as presented in Fig. 2 (a). Different colors stand for pH-dependent measurements at different salt concentration.

In fact, all shear moduli can be combined to a master curve by normalizing the angular frequency scale, see for example the blue symbols in Fig. 2 (b). To superimpose the spectra to a master curve, we also have to shift the spectra very slightly on the modulus scale. This additional shift can be attributed to the changing polymer density, see discussion above, but these shift factors $f_{G,pH}$ are very small as compared to the shift factors $f_{\omega,pH}$ for the frequency scale and will not be discussed here any further.

Figure 2 (b) shows additional sets of master curves that were obtained in an analogue fashion from pH-dependent G'' and G' spectra determined at other salt concentrations. The green symbols correspond to data of PEC coacervates where no extra KCl salt was added; red symbols are used for solutions with a KCl concentration of 0.5 mol/L. In all cases, the individual G' and G'' -spectra measured at different pH-values do form a master curve. The applicability of the scaling procedure implies that changes of the pH-value, analogue to changes of temperature, influence the rate of the underlying complex dynamics without changing the basic mechanism. The logarithms of the shift factors used to create the master curves are displayed in Fig. 3.

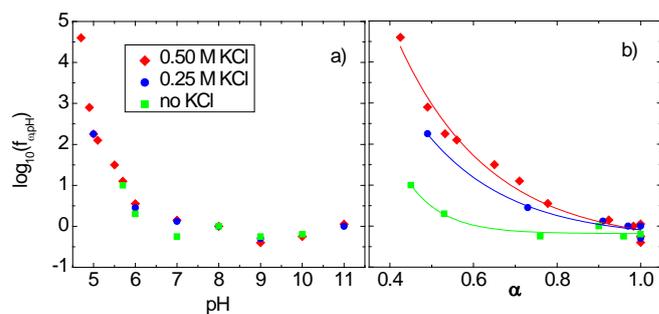


Fig. 3 Shift factors determined from superimposing individual $G'(\omega)$ and $G''(\omega)$ spectra to the master curves presented in Fig. 2 (b) plotted as a function of the dissociation constant of PAA. The lines are just guides to the eye.

We see in Fig. 3 (a) that there is a very strong decrease of $\log_{10}(f_{\omega,pH})$ between pH = 5 and pH = 7. Above pH = 7, the shift factors $f_{\omega,pH}$ are always close to one. The latter implies that for pH > 7 the position of the G' and G'' spectra on the frequency scale almost remains the same. In other words, there is a pH-regime in which the rate of the complex dynamics is very sensitive to pH-changes, whereas above pH = 7 it is not. The reason for this observation becomes clear when we regard the degree of dissociation, α , instead of the pH-value. According to Fig. 1, we see that even at a fixed pH-value, α of PAA can differ with varying KCl-concentration. Therefore, we now plot the same shift factors as a function of the degree of dissociation determined for solutions of the weak polyanions PAA at different salt contents, see Fig. 3 (b). We assume that changes in α due to complexation are negligible because we did not observe any changes of the pH-values after the pH-adjusted solutions of the polyanions and polycations were mixed to form the coacervate phase. Fig. 3 (b) shows that $\log_{10}(f_{\omega,pH})$ decreases significantly with the degree of dissociation and reaches finally a plateau regime at about $\alpha = 0.9$. This means that indeed the degree of dissociation is the crucial property determining the coacervate dynamics. Once the PAA is (almost) fully charged, the dynamics (as probed by the shear moduli G'' and G') are not changed any further on increasing the pH value. The decay is the more pronounced the higher the salt content is: $f_{\omega,pH}$ changes by five orders of magnitude at a salt concentration of 0.5 M KCl whereas it decreases only by one order of magnitude in the coacervates without added salt.

In order to explain these findings we have to look at the underlying dynamics which governs the frequency-dependent shear moduli G' and G'' , respectively. At high pH-values, the PAA polyanions are fully charged. PEC are formed because of the strong Coulombic interactions between the opposite charges on the polycations and polyanions. These bonds, however, are not to be considered as rigid, but they can be opened and reformed, as also described in the work of Spruijt et al.^{10,11}. They concluded that the ionic bonds between the oppositely charged polyion chains act as temporary cross-links. Addition of salt influences the bond energy of all ionic

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bonds to the same extent, so that all relaxation modes are shifted equally^{10,11}.

In our case (which differs from the cited literature as the charge density on the polymeric chains can change with pH) we are able to probe the chain dynamics even in the absence of salt. Addition of salt accelerates the chain dynamics for two reasons: First, the small cations and anions of the added salt themselves can act as (extrinsic) charge compensators for the opposite charges on the polyions. This reduces the binding strength between the oppositely charged polyions resulting in faster dynamics. In addition, it is evident from the volume of the coacervate phase that the presence of salt also increases the amount of water absorbed into the complex. The water, incorporated into the hydrophilic segments of the complex, acts as a plasticizer and therefore also accelerates the chain dynamics. Uncharged hydrophobic segments of the PAA chain may play an important role. A reduction of the charge density of the weak polyions resulting from a pH decrease enlarges the average distances between the negative charges of the dissociated groups on the PAA chains which goes hand in hand with an increasing length of uncharged chain segments with partially hydrophobic properties located between the negative charges. We may speculate that the formation of uncharged hydrophobic chain loops between the charged binding sites on the polyions apparently reduces the rate of the chain dynamics tremendously, possibly due to hydrophobic interactions. In spite of the ionic character of polyelectrolyte complexes, it was shown that hydrophobic interactions may play a large role in polyelectrolyte complexation¹⁶. This effect is, however, less pronounced in PEC coacervates without additional salt, where the dynamics is slow even in the completely dissociated state. In other words, the “disturbance” of the polyanion/polycation dynamics resulting from the formation of uncharged polymer loops is the more pronounced the faster the dynamics in the “undisturbed” complex is. The deceleration by charge dilution occurring on pH reduction, however, is due to an analogue reduction of interactions between all types of charges. Therefore, the G' and G'' -spectra are only shifted with respect to each other on the frequency scale, but their spectral shapes do not change, establishing the scaling properties in the novel time-pH superposition principle.

Finally, in order to test whether our coacervates also obey the time-salt superposition principle reported by Spruijt et al.^{10,11} we tried to superimpose the three individual master curves of Fig. 1 (b) to a super master curve. The result is shown in Fig. 4, where the inset summarizes the shift factors $f_{\omega,c}$ for creating the super master curve as a function of salt concentration. Indeed, the validity of the time-salt superposition principle also holds for our complexes. The exact dependence of our shift factors on the ion concentration differs however from that reported in references [10,11]. This shows that the dependence of dynamical properties on salt concentration is influenced by the type of polyelectrolytes.

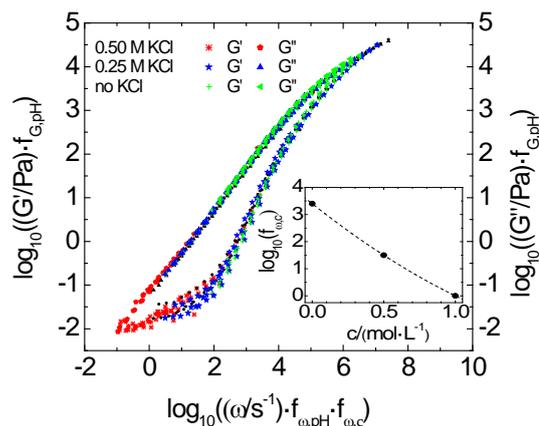


Fig. 4 Super master curve resulting from the individual master curves as displayed in Fig. 2 (b). The inset shows the shift factors used for this scaling procedure. The dashed line is just a guide to the eye.

In summary, we have shown that the dynamics in polyelectrolyte complex coacervates is strongly influenced by the presence of salt and by the average distance of charged groups on the polyelectrolyte chains. Both effects can be separated from each other by a two-step-procedure. First, G' and G'' -spectra taken at different pH-values (and therefore different degrees of dissociation) but constant ion content are normalized to form a master curve. This procedure allows determining of how the PEC dynamics is influenced by the average distance of the charged groups on the polyelectrolyte chain. In a second step, the so formed master curves taken at different ion contents are additionally normalized with respect to each other to form a super master curve. This procedure allows determining the effect of salt ions present in the coacervate phases. In all cases we find that the position of the spectra on the frequency scale changes, but not the shape of the G' and G'' -spectra. This implies that the charge density of the PE chains and the salt ions both influence the rate of the complex dynamics strongly, but not the basic mechanism of temporary bond formation and bond opening between the charges. The decrease in the number of charged groups on one type of polyion increases the length of uncharged hydrophobic chain loops, which reduces the rate of the chain dynamics tremendously. This is even more interesting, as the type of interactions involved do vary, whereas the dynamic mechanisms determining the spectral shape remain invariant. The deceleration of dynamics is less pronounced in PEC coacervates without additional KCl salt, where the dynamics is slow even in the completely dissociated state. This implies that the “disturbance” of the polyanion/polycation dynamics resulting from the formation of uncharged polymer loops is the more pronounced the faster the dynamics in the “undisturbed” complex is.

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