

Rheological properties of aqueous solutions of cetylpyridinium chloride in the presence of sodium chlorate

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Abstract We have studied the effect of salt content on the linear viscoelastic properties of wormlike micelles formed from cetylpyridinium chloride in the presence of the nonpenetrating inorganic salt, sodium chlorate. Rotational rheometry and oscillatory squeeze flow were used to determine the shear moduli G' and G'' in the angular frequency range from 0.1 rad s⁻¹ up to 10⁴ rad s⁻¹. From G' and G'' data, we deduce the zero-shear viscosity η_0 , relaxation time T_R and plateau modulus G_0 . With regard to increasing salt concentration, at fixed surfactant concentrations of 0.3 and 0.6 M, we observe a maximum of η_0 as well as of T_R , whereas G_0 increases continuously with ionic strength. This result is different from that obtained by Cappelaere and Cressely (Rheol Acta 39:346–353, 2000), who studied the same salt/surfactant system. They report a strong decrease of G_0 with ionic strength at salt concentrations higher than that corresponding to the viscosity maximum and explained this decrease by a progressive diminution of the micellar length. We expect an inaccuracy of their oscillatory shear measurements in the high-frequency regime ($100 < \omega < 250$ rad s⁻¹) to be responsible for an incorrect estimation of G_0 and, consequently, a flawed interpretation of the viscosity decline.

Keywords High-frequency rheology · Micellar solutions · Salt effect

Introduction

In an aqueous solution, surfactant molecules assemble reversibly into a variety of spatially organized structures, whose common feature is the tendency for their hydrophobic tails to avoid contact with water. In the case of charged surfactants, the area per polar head depends strongly on the nature of the counterions and, more specifically, on their ability to bind to the surfactant molecules. An easy way to induce a morphological variation, for example, from spherical micelles to cylindrical micelles, is to decrease the effective head-group area by adding salt, which screens the electrostatic repulsions between the head groups and allows them to approach. Hence, under appropriate conditions for concentration, salinity, temperature, presence of counterion, and so on, surfactants will self-assemble into flexible cylindrical micelles, termed wormlike micelles. These wormlike micelles can become entangled even at fairly low concentrations, and their behavior shows strong parallels with conventional polymer chains, but they have larger diameter (~1–10 nm) and a longer persistence length (~10–100 nm). Small changes in surfactant structure and counterion nature (Porte and Appell 1984) or concentration, added electrolytes, and temperature can drastically alter the length, flexibility, and interactions of micelles, which results in significant effects on the macroscopic rheological properties. In particular, several systems formed by ionic surfactants and inorganic salts show a pronounced maximum of the zero-shear viscosity as the salt concentration increases

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(Candau et al. 1993; Khatory et al. 1993; Cappelaere and Cressely 1998, 2000; Raghavan and Kaler 2001; Schubert et al. 2003). This viscosity maximum can be attributed to the transition from linear to branched micelles. For those systems, the variation of the plateau modulus G_0 near the maximal viscosity is almost independent of salt concentration, but in some specific cases, G_0 increases at very high-salt content (Oelschlaeger et al. 2010). This increase can be attributed to an additional contribution of branching points to the cross-link density. Only one literature study shows an opposite behavior for the variation of G_0 beyond the viscosity maximum. Cappelaere and Cressely (2000) report a strong decrease of G_0 at salt concentrations larger than that corresponding to the viscosity maximum for the cetylpyridinium chloride (CPyCl)/sodium chlorate (NaClO_3) system at a constant surfactant concentration of 0.3 M. They interpret this G_0 decrease as a progressive diminution of the micellar length. We, however, expect an inaccuracy of their rotational rheometry measurements in the high-frequency regime ($100 < \omega < 250 \text{ rad s}^{-1}$) to be responsible for an incorrect estimation of G_0 and, consequently, the mistaken interpretation of the viscosity decrease. In our study we have used oscillatory squeeze flow measurements to more precisely determine the plateau modulus G_0 from G' data at frequencies between 10 and 10^4 rad s^{-1} . We investigated the CPyCl/ NaClO_3 system at a surfactant concentration of 0.3 M as well as at a higher surfactant concentration of 0.6 M in order to shift the entire viscoelastic spectrum to lower frequencies. In this case, the plateau modulus can be assessed with much better accuracy.

Materials and methods

Sample characteristics

CPyCl and NaClO_3 are commercially available; they were purchased from Carl Roth GmbH (Karlsruhe, Germany). Aqueous solutions of different NaClO_3 /CPyCl ratio at constant surfactant concentration of 0.3 and 0.6 M were prepared by gently stirring the surfactant and salt in deionized water. For equilibrium measurements, they were stored for at least 1 day at $T = 32^\circ\text{C}$. All rheological measurements were performed at this temperature as well.

Rotational rheometry

A rotational rheometer, Rheoscope 1 from Thermo Haake, equipped with a cone-plate measuring cell

(diameter $d = 60 \text{ mm}$, cone angle $\alpha = 1^\circ$) was used to perform static and small amplitude oscillatory shear experiments. In the latter, the frequency range was varied from 0.1 to 215 rad s^{-1} at a strain amplitude $\gamma_0 = 1$. Strain sweep experiments performed prior to the frequency sweeps confirm that this strain amplitude is sufficiently small to provide a linear material response at all investigated frequencies. A solvent trap was used to avoid the evaporation of the sample during the experiment.

Squeeze flow

Oscillatory squeeze flow experiments were performed using a piezo-driven axial vibrator (PAV) customized at the Institute for Dynamic Material Testing (Ulm, Germany). The general theory of squeeze flow is covered in standard textbooks of fluid mechanics (cf. Bird et al. 1987). The theory of the PAV and the mechanical and electronic setup used here are thoroughly discussed elsewhere (Oelschlaeger et al. 2009; Crassous et al. 2005; Kirschenmann 2003) and therefore summarized here only briefly. In our squeeze flow experiments, the samples are placed into a gap between two stainless steel plates. The lower plate is supported by a thin-walled quadratic copper tube carrying the piezo elements, which exert the vibrational motion and pick up the response signal. This lower part of the device is surrounded by a double-walled cylinder allowing for circulation of a thermostating fluid where the sample temperature is controlled with an accuracy of $\pm 0.1^\circ\text{C}$. The upper boundary of the gap is a thick metal lid, which provides a complete sealing of the fluid. The instrument operates at a constant force amplitude, from the ratio of the dynamic displacement of the lower plate (amplitude $\sim 5 \text{ nm}$) with and without fluid; the complex squeeze stiffness K^* of the fluid is obtained, which is directly related to the complex shear modulus G^* (Kirschenmann 2003):

$$K^* = \frac{3\pi R^4}{2d^3} G^* \left/ \left(1 + \frac{\rho\omega 2d^2}{10G^*} + \dots \right) \right. \quad (1)$$

where ρ is the fluid density, R (here 10 mm) is the radius, and d is the height of the gap. The denominator in Eq. 1 is a series expansion taking into account the inertia of the fluid in the gap. The determination of G^* strongly depends on the exact knowledge of d , which is determined by calibration using Newtonian liquids with viscosities between 1 and 2,000 mPa·s. Gap heights between 39 and 50 μm have been used here, corresponding to sample volumes between 100 and 200 μl . Moduli G' or G'' in the range from 0.1 Pa to 10 kPa are accessible with the setup described here. For both shear

and squeeze flow measurements, an experimental error of 5% has been estimated from at least five repetitions of the experiments using fresh material in each case.

Experimental results and discussion

Salt effect on the zero-shear viscosity η_0

The zero-shear viscosity η_0 has been determined from steady shear measurements. Variations of η_0 versus added salt, at constant surfactant concentrations of 0.3 and 0.6 M CPyCl, are given in Fig. 1. We observe, for the system at CPyCl 0.6 M, a viscosity maximum ($\eta_0 \sim 16$ Pa·s) at a NaClO_3 concentration of ~ 0.5 M, which corresponds to a salt/surfactant ratio ~ 1 . For the system with CPyCl 0.3 M, the viscosity maximum occurs at salt/surfactant ratio ~ 1.3 but is much lower and reaches just ~ 2.7 Pa·s. This result is similar to that obtained by Cappelaere and Cressely (2000). Similar viscosity maxima upon addition of salt have been observed for many other micellar systems formed with nonpenetrating counterions: cetyltrimethylammonium bromide (CTAB)/KBr (Khatory et al. 1993), erucyl bis (2-hydroxyethyl) methylammonium chloride (EHAC)/KCl (Schubert et al. 2004; Croce et al. 2003), CTAB/ NaNO_3 (Kuperkar et al. 2008; Oelschlaeger et al. 2010), and CTAB/ NaClO_3 (Oelschlaeger et al. 2010). For those systems, η_0 values at the maximum are higher and reach ~ 100 Pa·s, although the surfactant concentration is slightly lower. These results indicate that the addition of NaClO_3 to the CPyCl solutions has

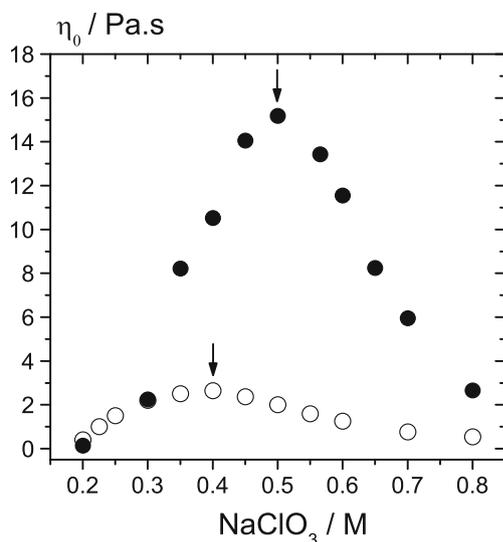


Fig. 1 Variation of the zero-shear viscosity η_0 as a function of salt concentration at a constant surfactant concentration CPyCl of 0.6 M (closed circles) and 0.3 M (open circles) as obtained from rotational rheometry measurements

less effect on the micellar structure and flow properties compared with the above systems. For systems with penetrating counterions, the viscosity values are even higher and can reach 10^3 – 10^4 Pa·s. (Oelschlaeger et al. 2009; Rehage and Hoffmann 1988; Raghavan and Kaler 2001). In general, the formation of the viscosity maximum with increasing salt concentration has been interpreted in terms of micellar branching, and for certain systems, this has been directly visualized by cryogenic-temperature transmission electron microscopy (cryo-TEM) imaging (Clausen et al. 1992; Croce et al. 2003). Nevertheless, it is not excluded that a reduction of the micellar length at high-salt concentrations can also explain the occurrence of a viscosity maximum.

Salt effect on the terminal relaxation time T_R

Different methods have been used to determine the terminal relaxation time. T_R has been obtained from rotational rheometry measurements as the reciprocal of the crossover frequency, at which $G' = G''$, but also from a fit of G' and G'' using the Maxwell model. In this case, G' and G'' are given by the following equations:

$$G'(\omega) = G_0 \omega^2 T_R^2 / (1 + \omega^2 T_R^2) \quad (2)$$

and

$$G''(\omega) = G_0 \omega T_R / (1 + \omega^2 T_R^2) \quad (3)$$

Figure 2 shows an example of Maxwell fits for three different wormlike micelles (WLM) solutions: at low-salt content (0.3 M) below the viscosity maximum, at salt concentration (0.5 M) corresponding to the viscosity maximum and at high-salt content (0.7 M) beyond the maximum. In all cases, this single-mode Maxwell model describes experimental results in the terminal flow regime very well. Finally, T_R was also determined as the reciprocal of the crossover frequency obtained from oscillatory squeeze flow measurements. Figure 3 shows the variation of G' and G'' as a function of frequency as determined from rotational and squeeze measurements at NaClO_3 concentration of 0.4 M. Very good agreement is found between both techniques; the shapes of the relaxation spectra coincide very well over the frequency range $10 < \omega < 200$ rad s^{-1} . The absolute values also agree very well, where these curves have not been shifted to match the data. The variation of T_R with addition of salt, determined from different methods, for 0.3 and 0.6 M CPyCl is shown in Fig. 4. In both cases, the variation of T_R as a function of salt concentration is qualitatively the same, independent of the technique used. The T_R dependence is similar to the dependence

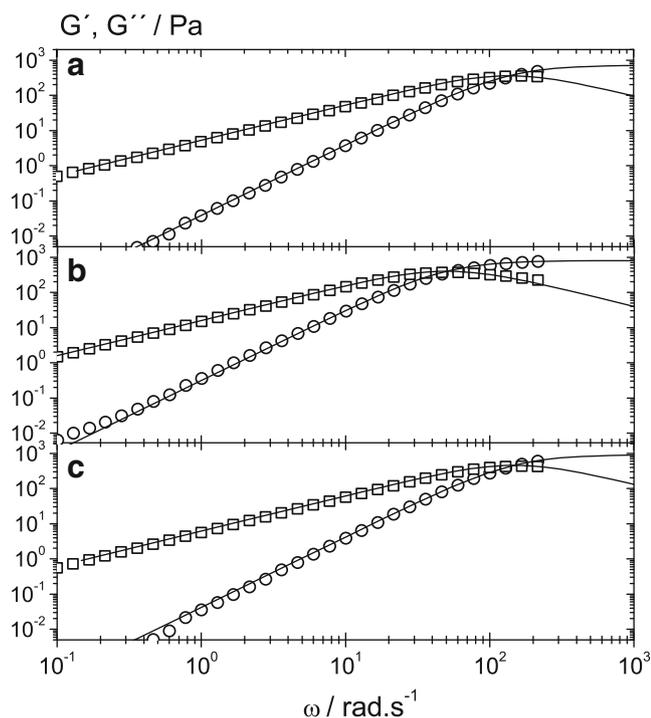


Fig. 2 Dynamic shear moduli G' and G'' for aqueous solutions of 0.6 M CPyCl/NaClO₃: **a** 0.3 M, **b** 0.5 M, and **c** 0.7 M obtained from rotational rheometry (G' open circles, G'' open squares). The solid lines represent the fit of G' and G'' using the Maxwell model

of η_0 , with both having a maximum at the same NaClO₃ concentration. Interpretations of these variations have already been discussed in many studies. The increase is due to an increase in the micellar length (Clausen et al. 1992), and the decrease can be explained by a decrease

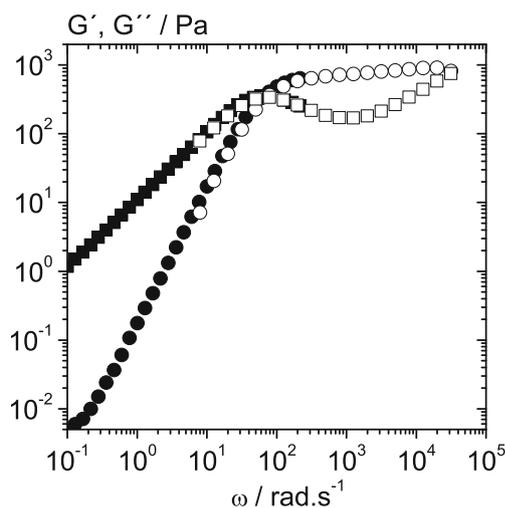


Fig. 3 Dynamic shear moduli G' and G'' for an aqueous solution of 0.6 M CPyCl/0.4 M NaClO₃ obtained from oscillatory squeeze flow (G' open circles, G'' open squares) and rotational rheometry (G' closed circles, G'' closed squares)

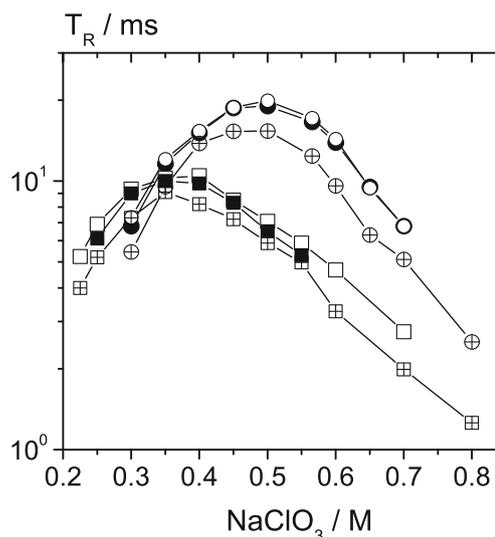


Fig. 4 Variation of the relaxation time T_R as a function of salt concentration at constant surfactant concentration of 0.6 M CPyCl as obtained from rotational rheometry (closed circles), Maxwell fit (open circles), and oscillatory squeeze flow (open circles with cross) as well for a concentration of 0.3 M CPyCl as obtained from rotational rheometry (closed squares), Maxwell fit (open squares) and oscillatory squeeze flow (open squares with cross)

in the mean size of the wormlike micelles or by the formation of branching points (Candau et al. 1993).

Salt effect on the plateau modulus G_0

Figure 5a and b shows the variation of the plateau modulus G_0 with addition of salt as determined from oscillatory shear and oscillatory squeeze flow measurements for systems with 0.6 and 0.3 M CPyCl, respectively. In both images, G_0 has been determined from rotational rheometry as two times the value of G^* , at the crossover frequency where G' and G'' cross each other, corresponding to the single-mode Maxwell model (closed circles), and from the Maxwell fit of G' and G'' (open circles). For oscillatory squeeze flow, G_0 has been determined from G'' min (closed stars), from $2G^*$ (closed squares), and from Maxwell fit (open squares). Although the absolute values of G_0 vary slightly depending on the measurement technique and the mode of data evaluation, the variation of G_0 always shows the same trend. We observe an increase in the plateau modulus at low-salt content corresponding to a strong increase of the zero-shear viscosity (solid line). This result is similar to that obtained by Cappelaere and Cressely (2000) and is due to the formation of and increase in the number of entanglements accompanying the growth of the micelles, where those micelles remain linear. The difference with Cappelaere

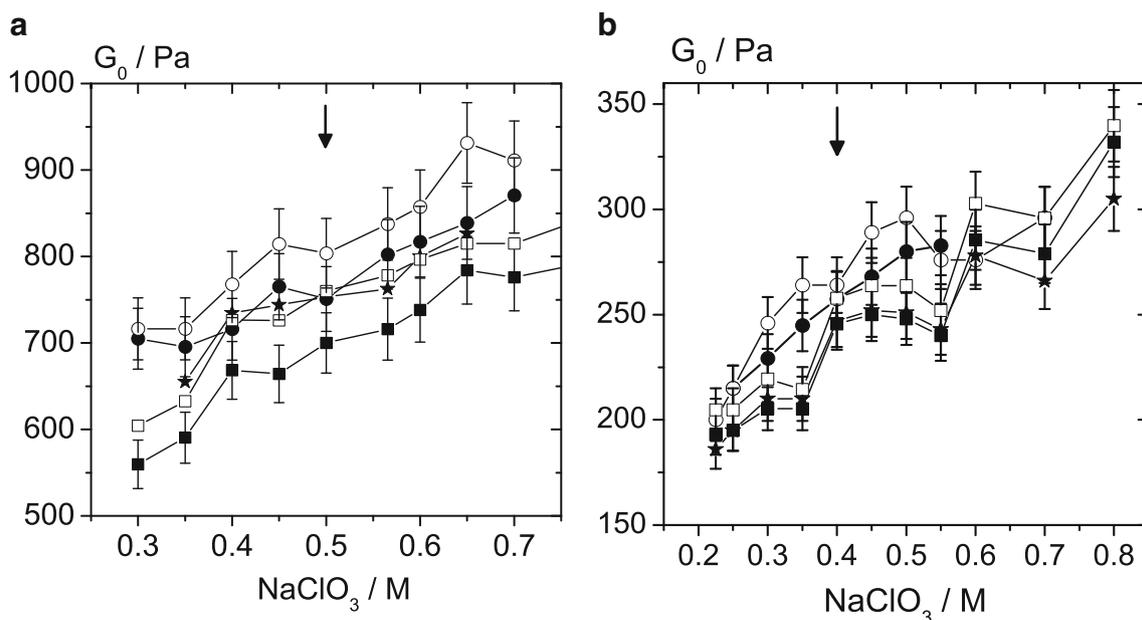


Fig. 5 Variation of the plateau modulus G_0 as a function of salt concentration at constant surfactant (CPyCl) concentration of 0.6 M (**a**) and 0.3 M (**b**) as obtained from: rotational rheometry from $2G^*$ (closed circles) and Maxwell fit (open circles); oscillatory

squeeze flow from G'' min (closed stars), from $2G^*$ (closed squares), and from Maxwell fit (open squares). The arrow represents the zero-shear viscosity maximum. Experimental errors of 5% for squeeze and shear measurements have been estimated

and Cressely (2000) resides in the variation of G_0 at salt concentration around and after the viscosity maximum. In our study and in all cases, we find that G_0 is almost independent of salt concentration around the viscosity maximum, but continues to increase at very high-salt content. This variation is significant as it is greater than the measurement uncertainty, and we can clearly see that G_0 does not decrease after the viscosity maximum. Conversely, Cappelaere and Cressely (2000) claim that G_0 continuously decreases as the ionic strength increases at salt concentrations higher than that corresponding to the viscosity maximum. They speculate that at excess salt content, the salt breaks the micelle network junctions and so reduces the micellar length and, consequently, the number of entanglements. We expect an inaccuracy of their rotational rheometry measurements in the high-frequency regime ($100 < \omega < 250 \text{ rad s}^{-1}$) to be responsible for an erroneous determination of G_0 . In general, results obtained by commercial rheometers are only reliable at frequencies up to 100 rad s^{-1} . However, for the system they have investigated with 0.3 M surfactant concentration, rotational rheometry just covers the onset of the plateau regime. For salt concentrations beyond 0.4 M, the crossover frequency is $>100 \text{ rad s}^{-1}$, and thus, any determination of G_0 is suspected to be erroneous. In our study, we used squeeze flow measurements covering the frequency range $6 \text{ rad s}^{-1} < \omega < 4 \cdot 10^4 \text{ rad s}^{-1}$ to determine G_0 . In this frequency

regime, the plateau modulus is very well defined with a high accuracy, and our experiments clearly show a monotonic increase in G_0 with salt concentration. This second G_0 increase may be attributed to the formation of branched micelles that give an additional contribution to the cross-link density. Indeed, it has been proposed that an increase of the elastic modulus can be a reliable indicator of branching (In et al. 1999; Danino et al. 1995; Kern et al. 1994; Karaborni et al. 1994; Bernheim-Groswasser et al. 2000). In addition, a good signature of the structure of the investigated system can also be provided by the volume fraction dependence of the zero-shear viscosity in the semidilute regime. For linear micelles, the Cates model (Cates 1987, 1988) predicts a scaling behavior $\eta_0 \sim \phi^{3.5}$. For a system consisting of linear and branched micelles, the Cates approach, modified by the Lequeux model for reptation of branched micelles (Lequeux 1992), predicts $\eta_0 \sim \phi^\alpha$ with $2.4 \leq \alpha \leq 3.5$. In our study, we found for the 0.6 M NaClO_3 system (beyond the viscosity maximum) a power law exponent α equal to 2.42. This result indicates that the system contains both end-caps and intermicellar connections. Previous light scattering and rheological studies performed by Candau et al. (1993), Khatory et al. (1993), and Appell et al. (1992) on a system formed from CPyClO₃ and NaClO_3 have shown similar exponent values at salt concentrations also beyond the viscosity maximum. The results were interpreted as corresponding to a structural change

upon increasing salt content from a system of entangled linear micelles to a system where cross-links or branchpoints resulting from local fusion of the micelles are formed.

Conclusion

In this study, we have used rotational rheometry and oscillatory squeeze flow to investigate the effect of salt on the rheological properties of the system formed from CPyCl and NaClO₃ in aqueous solution. The squeeze flow technique provides very precise G' and G'' data at frequencies between 10 and 10⁴ rad s⁻¹ and thus allows for an accurate, direct determination of the plateau modulus of these surfactant solutions. Upon increasing salt concentration, at a fixed surfactant concentration, we observe a maximum for η_0 and T_R , whereas G_0 increases continuously with ionic strength. This latter result is different from that obtained by Cappelaere and Cressely (2000), who reported a strong decrease of G_0 with increasing ionic strength at salt concentrations higher than that corresponding to the viscosity maximum. We expect an inaccuracy of their oscillatory shear measurements in the high-frequency regime to be responsible for an incorrect estimation of G_0 and consequently an erroneous interpretation of the viscosity decrease. The increase in G_0 observed in our study seems to be closely related to the formation of branched micelles, providing an additional contribution to the cross-link density. This interpretation is further supported by the power law exponent value of 2.42 found for the dependence of the zero-shear viscosity on surfactant concentration and by cryo-TEM images taken for the same salt/surfactant system, but at lower surfactant concentration.

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