Interaction between ethyl(hydroxyethyl)cellulose and sodium dodecyl sulphate in aqueous solution

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Abstract: Using sodium activity, viscosity, and cloudpoint measurements, it has been shown that sodium dodecyl sulphate (SDS) binds to ethyl(hydroxyethyl)cellulose in a cooperative manner. In the absence of salt the binding leads to an increase in the clouding temperature, but when a small amount of salt (0.01 molal) is present first a drastic decrease and then an equally drastic increase in the cloud point temperature is observed. The binding of SDS also initially leads to an increase in viscosity followed by a decreased viscosity at higher SDS concentrations. A molecular mechanism explaining the observed behavior is given.

Key words: Nonionic polymer, ionic tenside, sodium activity, clouding temperature.

Introduction

Ethyl(hydroxyethyl)cellulose (EHEC) is a neutral cellulose ether manufactured from cellulose by substitution with ethyl and ethyleneoxide groups. EHEC has a wide applicability in colloid chemistry; it acts as a thickening and dispersing agent in waterbased paints and as an emulsifying agent in foodstuffs and pharmaceuticals, for example. However, in some cases strong unwanted interactions between EHEC and other components (e.g., surfactants) occur in the systems. This has been observed through, inter alia, a change in viscosity and, under certain conditions, a phase separation. In order to eliminate such problems in applications, it is important to characterize and understand the phase behavior in simpler, well-defined systems. Thus, we have previously reported cloud point (CP) and viscosity data of the four-component systems of EHEC, NaCl, either cetyltrimethylammonium bromide or sodium dodecyl sulphate (SDS), and water [1,2]. The temperature dependent solubility of EHEC, as reflected in changes of the CP, is affected by both anionic and cationic surfactants. If a long-chain ionic surfactant is added to a salt-free EHEC solution, the CP increases, i.e., the solubility of EHEC is enhanced. When a small amount of electrolyte is present, typically 0.01 molal, the CP curve displays a minimum as a function of surfactant concentration. The depth of the minimum is strongly dependent on the concentration of the electrolyte, but is more or less independent of the nature of the salt, when comparing ions having the same valency [2]. Adding salt alone also affects the CP of an EHEC solution, but only at concentrations that are orders of magnitude higher than those causing dramatic effects in the presence of ionic surfactant; to cause a salting-out effect of 20 °C by NaCl, a concentration of 1 molal is required.

In this work we have extended these studies on EHEC systems, utilizing the same techniques as mentioned above, together with sodium activity measurements and measurements of the partitioning of SDS and NaCl after phase separation. Furthermore, the spectral change of a coloring agent (pinacyanol iodide) added to EHEC-SDS solutions was examined. A mechanism will be proposed, which is comprised of both conformational changes of the polymer and a screening effect of the interactions between the polymer-surfactant complexes by added salt.

Experimental

Materials

EHEC powder (Bermocoll E 351 X) was supplied by Berol Kemi AB, Sweden (from the same batch previously used [1, 2]). On the average each anhydroglucose unit in cellulose was substituted with 0.9 ethyl group and 2.1 ethyleneoxide groups. The viscosity of a 1 % solution at 20 °C was 267 mPas (Brookfield LV, 12 rpm). The viscosity average molecular weight was 146 000, which corresponds to a degree of polymerization of about 520. The CP of a 1 % EHEC solution was 70 °C. The NaCl content in the dry powder was 5.2 %. SDS was obtained from BDH, England (specially purified for biochemical work).

Procedures

Desalted EHEC solutions were prepared by dialysis against membrane-filtrated water (Millipore, USA). As dialyzing membrane regenerated cellulose with a molecular weight cutoff of 6 000 was used, either as tubings or hollow fibers (Spectrum Medical Industries, USA). The Na content in the dialyzed EHEC solutions was analyzed by atomic absorption spectroscopy and was found to be less than 0.5 μg/ml.

Samples were prepared by weighing the components. The EHEC concentration is expressed in percent by weight and SDS and NaCl concentrations either in moles per kilogram EHEC-H_2O solution (molal) or moles per liter (M) EHEC-H_2O solution.

CP measurements were performed by visual observation in glass tubes. After heating the samples above the clouding temperature, the CP was taken as the temperature where the last visible sign of clouds disappeared on cooling (normally the CP value obtained on heating was 2–3 ° higher). The cooling rate was approximately 2 ° per min.

Viscosity measurements on concentrated EHEC solutions (0.5–2.0 %) were carried out with a Bohlin Rheometer System (Bohlin Reologi, Sweden). The instrument was equipped with a concentric cylinder with a radius of 12.5 mm (C 25). Temperature was kept constant at 20 °C. Viscosity vs. shear rate was recorded at different SDS additions, and the results are reported as relative viscosity at a specific shear rate, η/η_0, where η_0 is the viscosity of the EHEC solution without SDS. Viscosity measurements on 0.2 % EHEC solutions were performed by a glass capillary viscometer with an inner radius of 1.0 mm at 25 °C.

Spectrophotometrical determination of SDS concentration was performed according to [3, 4]. A methylene blue-dodecyl sulphate complex was formed in aqueous phase and extracted to methylene chloride. The absorbance of the organic phase was measured at 653.5 nm on a Lambda 3 spectrophotometer (Perkin-Elmer, USA).

The color change of pinacyanol iodide (Fluka, FRG) induced by SDS micellization with and without EHEC was visually studied at room temperature [5].

Sodium activity measurements were performed by a Na specific glass electrode and a double-junction reference electrode (model 97-11 and 90-02, respectively; Orion Research, USA). 3 M NH_4NO_3 was used as outer filling solution in the reference electrode [6]. The procedure roughly corresponds to the one in [7]. Water and EHEC-water solutions were titrated with a concentrated SDS solution, and the Na^+ activity was successively measured. During the measurements, the electrodes were not removed from the test solution. A low EHEC concentration (0.2 %) was
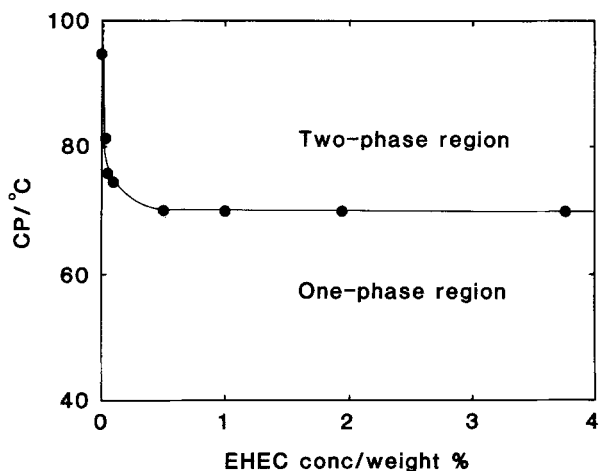

Fig. 1. Cloud point vs the EHEC concentration

employed to facilitate the mixing during the titration. All the sodium activity experiments were performed at 20 °C.

Results

CP in EHEC-water solutions

Presented in Fig. 1 is part of the phase diagram for the EHEC-water system. When the EHEC solution is heated above the lower critical solution temperature, i. e., the CP, the polymer precipitates, resulting in a cloudy solution and a loss in viscosity. The clouding manifests a phase separation into one polymerrich phase and one water phase containing almost no polymer. The former phase could be considered as a hydrated solid. From 0.5 % up to at least 4 % EHEC the CP is constant at 70 °C. On heating a concentrated EHEC solution a thermal gelation is observed, commonly referred to as a white gel-formation. The same phase characteristics have been observed for other cellulose ethers as well, such as for methylcellulose [8] and hydroxypropylcellulose [9].

Addition of SDS

In Fig. 2, the CP values are presented for an 1.0 % EHEC-water solution at different SDS concentrations. The EHEC solution was prepared from technical EHEC powder and therefore contained 0.0089 M (0.052 %) NaCl. The curve reflects very well the synergistic surfactant-electrolyte effect observed for EHEC solutions: When a relatively small amount of salt is present the addition of ionic surfactant initially
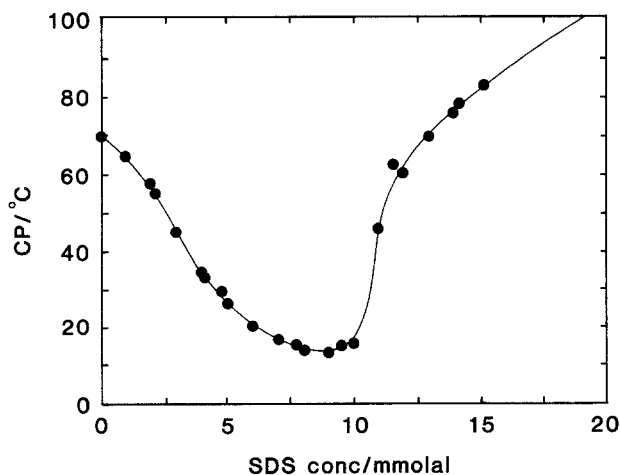
Fig. 2. Cloud point of an 1.0% EHEC-water solution containing 0.0089 M NaCl vs the SDS concentration

causes a CP depression. In the present case the CP decreases by more than 50 °C at low SDS concentrations. Here the clouding, or more correctly the haziness, is followed by a separation into two liquid phases. At further SDS additions the CP increases and at concentrations higher than 0.02 molal the clouding occurs above 100 °C.

The NaCl dependence

The depth and width of the CP minimum in Fig. 2 are very dependent on the salt concentration [1,2]. A NaCl content of only 0.002 M corresponds to a CP depression of 20 °C. At NaCl concentrations higher than 0.010 M, the CP minima are located below 0 °C. This is shown in Refs. [1] and [2] where 0.002–0.019 M NaCl has been added to 0.9% EHEC-water solutions before the addition of SDS. Without surfactant, the presence of 0.002–0.019 M NaCl has no significant effect on the CP, i.e., for EHEC solutions containing these amounts of NaCl the CP is invariant at 70 °C. In the salt-free case, the CP curve also possesses a CP minimum, although small, which could be explained as an effect of the relatively high critical micelle concentration (CMC) of SDS (0.0081 M at 25 °C). A fairly high amount of free surfactant ions and counterions is then present in the solution; these ions would screen the repulsive interactions between charged polymer chains in a manner similar to ordinary electrolytes (vide infra).

The EHEC concentration dependence and viscosity effects

In Figs. 3a–c, the relative viscosity measurements (open circles) and the CP measurements (filled circles) for EHEC solutions are presented as a function of the SDS concentration. Three EHEC concentrations were investigated: 0.2% (Fig. 3a), 0.5% (Fig. 3b), and 2.0% (Fig. 3c). Measurements on 0.9% EHEC solutions are presented in [1,2]. For the most diluted system, the viscosity was measured by a glass capillary viscometer at 25 °C, while for the other systems a rotating concentric cylinder instrument was employed at 20 °C. The system in Fig. 3a corresponds to a salt-free EHEC solution, while the systems in Figs. 3b and 3c correspond to EHEC solutions which were prepared from technical substance and therefore contained NaCl. The NaCl content in these systems was 4.4 (3b) and 17.8 mM (3c), respectively.

The SDS addition results in a considerable rise in viscosity, both with and without NaCl. The maximum value of η/η_0 increases with the polymer concentration: for the 0.2% EHEC solution the viscosity increase is only 10% while for the 2.0% solution the increase is fivefold. Furthermore, an increase in EHEC concentration leads to a displacement of the viscosity maximum to higher surfactant concentration. Further addition of SDS results in a drastic decrease in the viscosity, and in all cases η/η_0 is well below unity at high SDS concentration. The two-phase region is extended when the EHEC concentration is increased and this is especially pronounced when NaCl is present. For the 0.5% and 0.9% EHEC solutions the CP minima are below 0 °C, whereas for the highest concentration the minimum is located at room temperature. The CP minima are correlated with the positions of the maxima in η/η_0, but somewhat shifted to lower SDS concentrations. (Again, relatively small CP minima for the salt-free systems (0.2% and 0.9% EHEC) are observed.)

Partitioning of SDS, NaCl, and EHEC after phase separation

An important question relates to the partitioning of the components between the liquid phases above the critical point. 1.0% EHEC solutions with 0.0089 molal NaCl and with different additions of SDS were heated to 50 °C. At this temperature a phase separation occurs for SDS concentrations from 0.003 to 0.011 molal. The system separates into one polymer-depleted phase (A) and one polymer-rich phase (B) and in the former phase the SDS concentration was determined spectro-

a)

Fig. 4. Analyzed SDS concentration in the water-rich phase A after separation at 50 °C vs the total SDS concentration
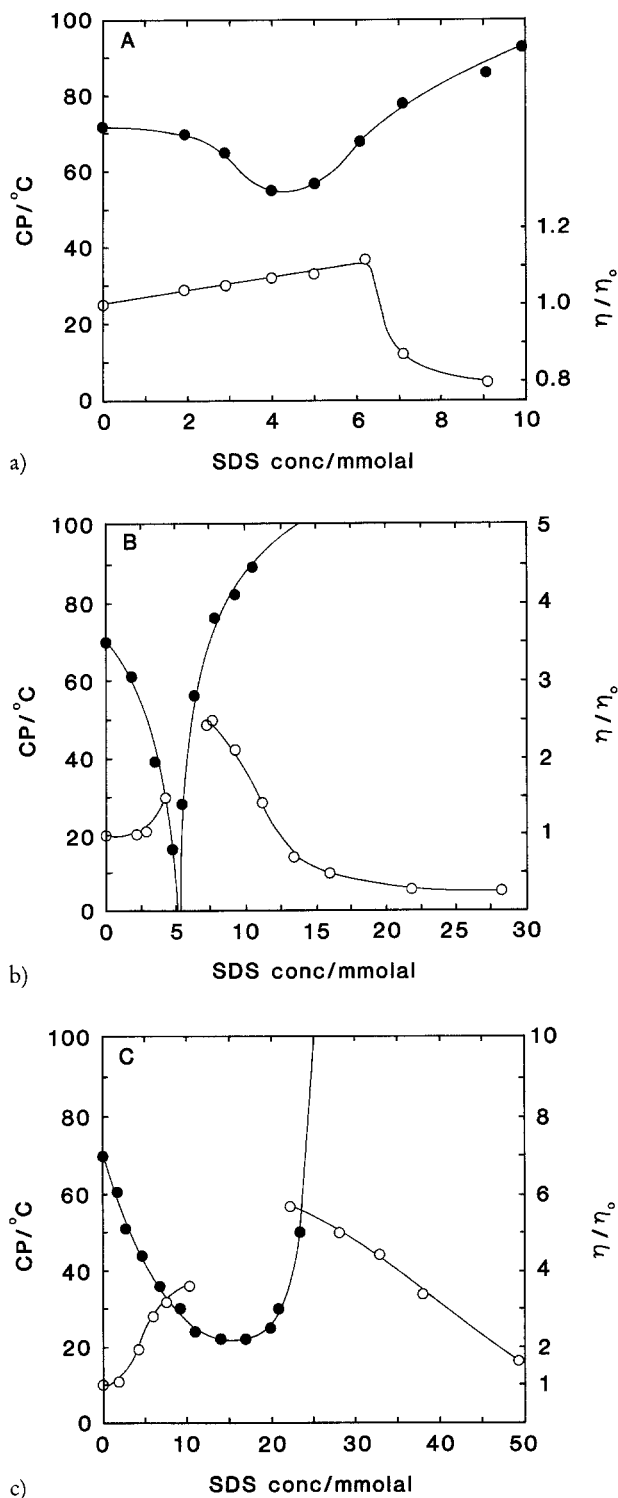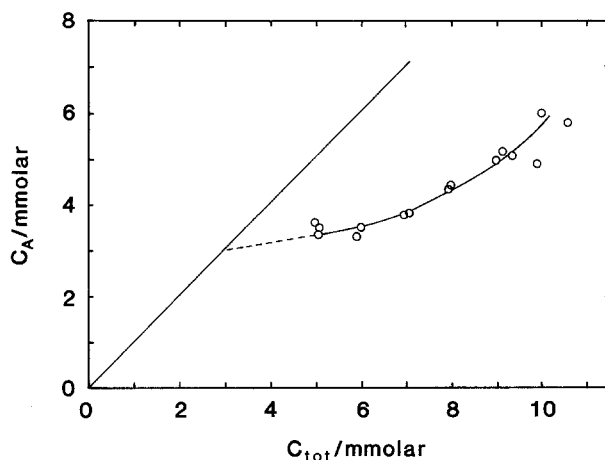

b)

c)

Fig. 3. Cloud point (left; filled circles) and relative viscosity at 20 °C (right; open circles) for EHEC-water solutions vs the SDS concentration: a) 0.2 % EHEC without salt; b) 0.5 % EHEC, C_{NaCl} = 4.4 mM (shear rate = 148 s^{-1}); c) 2.0 % EHEC, C_{NaCl} = 17.6 mM (shear rate = 2.34 s^{-1})

photometrically. Presented in Fig. 4 are the analyzed SDS concentrations in phase A versus the total SDS concentration in the system at 50 °C. In addition, summarized in Table 1 are the compositions of phase A and B, respectively, for an addition of 0.0060 molal SDS to the original EHEC solution. Obviously the phase separation is combined with an enrichment of the surfactant in the polymer-rich phase. The Na concentration in phase A (determined by AAS) is the same as in the original EHEC solution and thus the salt is equally partitioned between the phases. The EHEC concentration in phase A, determined by freeze-drying, was 10 times lower than in the polymer-rich phase.

Addition of pinacyanol iodide

When pinacyanol iodide is incorporated into micelles a color change of the micellar solution from red to blue occurs [5]. For an SDS solution at room temperature this is observed at a concentration of

Table. 1. Composition of the phases after separation at 50 °C of a system initially containing 1.0 % EHEC, 0.0060 molal SDS, and 0.0089 M NaCl

Phase	Volume fraction	EHEC conc./%	[DS$^-$]/M	[Na$^+$]/M	[Cl$^-$]/M
A	0.7	0.21	0.0035	0.0124	0.0089[a]
B	0.3	2.8	0.012[a]		

[a] calculated

6 mM, while for salt-free 0.5 % and 0.9 % EHEC solutions the blue shift appears already at an SDS concentration of 3.5 mM. The same result is obtained for undialyzed EHEC solutions. If the reagent is added to an EHEC solution without SDS, no color change is observed. Similar observations have been made for pinacyanol chloride added to aqueous poly(vinyl pyrrolidone) SDS solutions [5].

Sodium activity measurements

In Fig. 5, the Na^+ activity measurements are presented as a function of the SDS concentration. Circles represent the water-SDS system and triangles the water-0.2 % EHEC-SDS system. The curve for the former system changes slope at the CMC of SDS due to a relatively high concentration of Na^+ ions close to the micellar interface, thereby decreasing the activity in the bulk solution [10]. If 0.2 % EHEC is present in the system a somewhat different behavior is observed. The slope of the curve starts to decrease at a SDS concentration of about 5 mM, and above about 15 mM the curve has attained the same slope as above the CMC of the water-SDS system, i. e., two slope changes can be observed in the presence of polymer. These points can be identified with the two characteristic concentrations T_1 and T_2 in nonionic polymer-ionic surfactant systems [11]. T_1 corresponds to the onset of binding of surfactant to the polymer; T_1 is always lower than CMC and independent of the polymer concentration provided the molecular weight is high enough. T_2 is the concentration where free micelles start to form and

is dependent on the polymer concentration. Thus, if this description is applicable to our particular system, SDS starts to bind to EHEC at 5 mM and at 15 mM normal micelles start to form. NaCl additions to concentrations of 2–9 mM have no significant effect on the result (except for an increase in the absolute values of $a_{Na}+$), i. e., T_1 and T_2 are observed at the same SDS concentrations. However, a phase separation is observed in the region 5–15 mM SDS if a sufficient amount of NaCl is present during the titration. More precise measurements of T_1 and T_2 by other techniques are in progress.

Discussion

Before discussing the molecular interactions governing the phase behavior of the water-EHEC-ionic surfactant-salt system in general, the simpler and extensively studied system water-poly(ethyleneoxide) (PEO) will be considered. PEO clouds at a temperature somewhat higher than for EHEC of the present study. For the clouding process of PEO there exist competing theories in the literature; one ascribes the effect to a break-down of structured water around the PEO chain [12] one discusses hydrogen bonding between PEO and water [13], while an other points out that the phase behavior could be explained as a consequence of the conformational equilibria of the PEO chains [14,15]. However, a common feature in all models is a greater attraction between the PEO chains at elevated temperatures. In the more recent model this phenomenon is ascribed to an increase in the nonpolarity of the segments in the PEO chain, which results in an unfavorable interaction with the polar solvent water.

EHEC is made by substituting cellulose with ethyl and ethyleneoxide (EO) groups. By this chemical modification the stability of the crystalline cellulose fibers is reduced and thereby water solubility of the polymer chain is achieved. The cellulose fibers in their native form are known to be built-up from cellulose molecules in an ordered stretched-out or band-like conformation [16]. We suggest that the EHEC molecule mainly exists in a coil-like structure in aqueous solution. As the temperature is increased the EO groups of the EHEC molecules start to attract each other, and a phase separation occurs. It can be assumed that the cellulose backbone of the EHEC molecule in the precipitated state is in an ordered conformation, in analogy with cellulose.
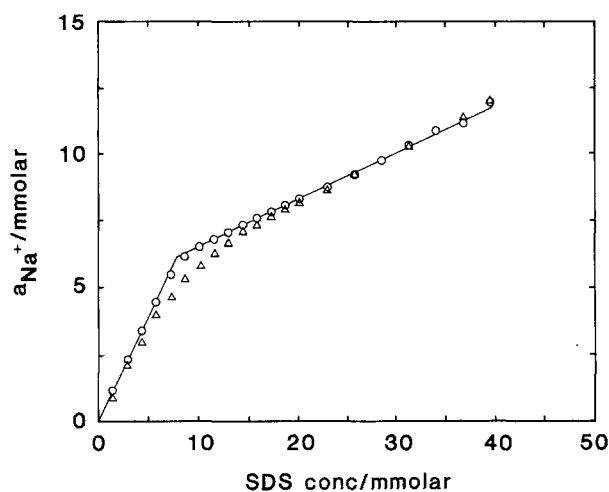

Fig. 5. Sodium activity vs the SDS concentration at 20 °C: (circles) SDS-water; (triangles) SDS-0.2 % EHEC-water

When an ionic surfactant like SDS is added to the EHEC-water system, the surfactant molecules form complexes with the EHEC polymer. This occurs at an SDS concentration somewhat lower than CMC, i. e., at T_1, which is supported by the color change of pinacyanol iodide and by the Na^+ activity measurements. As a consequence of the binding the EHEC molecules become charged and expand due to repulsion between the charged surfactant head groups, which is observed as an increase in viscosity. Furthermore, conformational changes are likely to occur due to an increased amount of nonpolar interaction between the EO and ethyl groups attached to the cellulose and the hydrocarbon tails of the surfactant. Without salt the charge repulsion leads to an even distribution of micelle-like aggregates over all polymer chains, and it is also strong enough to overcome the attraction between polymer chains in ordered conformation. The increase in charge also favors an increase in solubility and for long hydrocarbon chain ionic surfactants an immediate increase in CP is observed, while for surfactants with intermediate hydrocarbon chain length, eg., SDS, a small CP minimum is observed as discussed earlier.

However, in the presence of salt the importance of the electrostatic forces is reduced and the CP decreases at low surfactant concentration. When the temperature is high, i. e., close to CP for the system, a very small amount of SDS is enough to induce a phase separation; one may say that the solubility of SDS in the formed EHEC-rich phase is larger than in the original water-EHEC solution. The SDS-EHEC aggregate that is formed close to CP probably contains only a few SDS molecules and several EHEC chains. When the temperature is decreased, more SDS molecules are needed in order to stabilize the phase separation in which the polymer-rich phase B precipitates. This means that the formed aggregates contain more SDS molecules and less EHEC at lower temperature. Thus, one would expect that the characteristic concentration T_1, where the surfactant starts to bind in a cooperative manner to the EHEC polymer, should decrease with increasing temperature. In fact, this is in agreement both with the results from self-diffusion measurements made on the EHEC-water-dodecyltrimethylammonium bromide system [17] and measurements in progress on surfactant ion activity made in collaboration with Prof. K. Shirahama, Saga University, Japan.

At higher surfactant concentrations the electrostatic effects start to dominate even in the presence of salt, which is reflected as an increase in CP. Furthermore, when the surfactant concentration exceeds T_2, micelles start to form in the bulk solution and the system changes gradually, from being described as micelles bound to a stretched-out polymer chain, to a fairly disorganized polymer chain bound to the micellar surface (cf. the "necklace" model for polymer-surfactant complexes proposed by Shirahama et al. [18]). This results in a decrease in viscosity that has been observed experimentally.

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