

The shape, size and flow behaviors of micelle forming various synthetic tannin materials in aqueous solutions

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Abstract: The results of viscometric and optical microscopic studies indicated that both Syntan 25 and Syntan PUR in aqueous concentrated solutions (above their c.m.c. values) at 25 °C are spherical in shape. The size and other physico-chemical parameters e. g. Volumes of the aggregated particle M_v , Radius of gyration R_g , Hydrodynamic radius \bar{R}_h , Diffusion coefficient \bar{D} , and the Correlation times for aggregate rotation T_r , Translational diffusion T_D and effective aggregation time T_a have been derived on the basis of microscopic results. The viscosity data for both Syntan 25 and Syntan PUR were analysed in terms of Einstein equation, Moulik equation, Jones-Dole equation. It has been shown that Syntan PUR was more highly hydrated than that of Syntan 25 although the intrinsic viscosity $[\eta]$, of Syntan PUR is nearly 1.5 times greater than that of Syntan 25. The Flory-Huggins equation and Thomas equation has been compared in both the Syntans and it has been concluded that the Thomas' constant k_1 may be 12.50 for perfect spherical shape of the particle instead of 10.05 (which has originally been proposed by Thomas).

Key words: Syntans micelles, Shape, Size and flow, Correlation times, Hydrodynamic & optical studies, Viscosity equations.

Introduction

Over the years a considerable experimental literature on Synthetic tannin materials (Syntan) in aqueous solutions has been compiled with a view to understand their dualistic role [1]. In our previous studies we first investigated [2] whether Syntans form true solution or present as micelles in aqueous solutions and utilizing our concept [3], we were able to study the thermodynamics and aggregation of the system in order to investigate the effectiveness of various Syntans in various environments.

In the light of existing controversies as to whether the shape of nonionic surfactant Triton X-100 micelle is spherical or ellipsoid, we were first able to determine the exact geometry of that Triton X-100 micelles with the help of our independent knowledge of micellar hydration [4]. Utilizing the same independent knowledge [4], we have determined the geometry of nonionic Tweens (Tween 20 and Tween 80) micelles [5]. Although the investigation of size and shape of anionic surfactant, Sodium dodecyl sulfate micelles has recently been reported [6] employing most sophisticated quasielastic light scattering spectroscopic methods but the size, shape and hydration of Syntans

is on the other hand lacking. Therefore, the study of shape, size and hydration of Syntans is necessary with the system itself in considering the applied interest [1, 7] as well as fundamental surface-chemical standpoints.

In this paper, we first report experiments in which shape, size, hydration and other physicochemical properties of Syntans micelles are determined in their concentrated solutions at 25 °C with the application of hydrodynamic and optical microscopic studies. These measurements confirm that the shape of large Syntans micelles is spherical.

Experimental section

Materials and methods:

A. Preparation of Syntan PUR and Syntan 25: Phenol is sulphonated at 105–110 °C for 3 hours and cooled down to 60 °C. Urea was dissolved in equal amount of water and added to sulphonated phenol and condensed with formaldehyde at 60 °C for 5 hours. Additional phenol was added and heated to 60 °C for 1 hour and condensed again with formaldehyde. The mole composition of Syntan PUR are: Phenol 3.5 mole; H₂SO₄ 3 mole; Urea 1.5 mole; Formaldehyde 2 moles; Phenol 1 mole and Formaldehyde 1 mole. The method of preparation of Syntan 25 and compositions are almost similar to syntan PUR excepting that Chrome shavings are added (50% on the weight of phenol) and heated for 1 hour with phenol and condensed with formaldehyde.

Reagents and solutions:

The Syntans¹) prepared as above in our laboratory are anionic in nature. In case of Syntan PUR, 1M urea in water was used as the medium during the experiment. A very little amount of neutral Na₂SO₄ present in the Syntan was removed by treatment with solid Ba(OH)₂. The precipitated BaSO₄ was separated from the mother liquor by high speed centrifuge. Finally the solution was passed through a column of Dowex 50WX8 (H⁺ form) resin in order to remove Ba⁺. Double distilled conductivity water is used throughout the experiment.

The number average molecular weight (\bar{M}_n) of Syntan PUR and Syntan 25 are 12540 and 15120 respectively determined by Vapour pressure osmometric (301A VAPOUR PRESSURE OSMOMETER, HEWLETT, PACKARD) method. The osmometer was calibrated against aqueous glucose solutions.

B. Optical microscopic study: Two to three drops of Syntans were taken in the cavities of the cavity slides and were covered with thin (No. 0) cover-slips taking care that no air bubbles remained under the cover slips. They were examined using oil-immersion objective. The refractive index of the immersion oil was 1.510. The Brownian movement of the aggregated particles was observed and the measurements were taken after attaining the equilibrium by means of a calibrated eye-piece micrometer scale. The value of each division in the eye-piece micrometer scale was first determined by means of a calibrated stage micrometer scale. To minimise errors 25 reading for each type of particles were taken. In both the Syntans two types of particles were observed and their shape were spherical. The average radius of the particles has been given in table 1. The measurement of radius of the particle by microscopic method was accurate within ± 5 per cent. After measuring the diameter of the aggregated particles, the volume, M_v , of the spherical shape of that aggregated particle was calculated using the following equation,

$$M_v = \frac{4}{3} \pi R^3 \quad (1)$$

where R is the radius of the aggregated particle. For spherical shape of the particle, the hydrodynamic radius, R_h is assumed to be equal

to R , the radius of the particle. The radius of gyration R_g , was calculated for spherical shape using formula [6]

$$R_g = (3/5)^{1/2} R. \quad (2)$$

The average diffusion coefficient, \bar{D} , was calculated from \bar{R}_h using a formula analogous to the Stokes-Einstein relation for spherical particles [8]

$$\bar{D} = kT/f = kT/6\pi\eta\bar{R}_h, \quad (3)$$

where k is Boltzmann's constant, T is the absolute temperature, f is the frictional coefficient and η is the coefficient of viscosity of the solvent. For spherical micelles \bar{R}_h is the hydrated radius of the sphere, whereas for non-spherical micelles \bar{R}_h depends in a complicated way on the hydrated volume and shape of the particles through the orientational averaging. The \bar{D} values deduced from this equation (3) will not be substantially affected by intermicellar interactions under the conditions of the present experiment.

C. Determination of the correlation time for the micellar aggregated motion: From the known values of radius R of the aggregated particle, T_a , the effective correlation time of the aggregate can be calculated using the Stokes-Einstein relation [8]

$$T_r = 4 \pi R^3 \eta / (3kT) = M_v \eta / (kT) \quad (4a)$$

$$\begin{aligned} T_D &= R^2 / (6\bar{D}) = R^2 / (6kT/f) \\ &= R^2 f / (6kT) = R^2 6\pi\eta R_h / (6kT) \\ &= \pi R^3 \eta / (kT) = \frac{3}{4} M_v \eta / (kT) = \frac{3}{4} T_r \end{aligned} \quad (4b)$$

$$\begin{aligned} 1/T_a &= 1/T_r + 1/T_D \\ T_a &= \frac{T_r \cdot T_D}{T_r + T_D} \end{aligned} \quad (4c)$$

Table 1. The results of radius, aggregated volume, radius of gyration, hydrodynamic radius, diffusion coefficient and correlation times for Syntan 25 and Syntan PUR in aqueous solution at 25 °C^a)

Radius (Å °)	$M_v \times 10^{16}$ (ml)	R_g (Å °)	\bar{R}_h (Å °)	$\bar{D} \times 10^7$ (cm ² ·sec ⁻¹)	$T_r \times 10^5$ (secs.)	$T_D \times 10^5$ (secs.)	$T_a \times 10^5$ (secs.)
SYNTAN 25							
450-990 (1125-1575)	3.82-40.62 (59.61-163.57)	348.6-766.8 (871.4-1220.0)	450-990 (1125-1575)	0.543-0.247 (0.217-0.155)	8.286-88.24 (129.48-355.3)	6.215-66.13 (97.210-266.73)	3.55-37.8 (55.52-152.4)
SYNTAN PUR							
270-675 (900-1350)	0.82-12.88 (30.52-103.01)	209.1-522.8 (697.1-1045.7)	270-675 (900-1350)	0.905-0.362 (0.272-0.181)	1.789-27.96 (66.29-223.74)	1.34-20.98 (49.63-176.8)	0.766-11.98 (28.38-95.89)

^a) The particles observed in the aggregates whose range has been specified in table 1. The results of bigger size particle has been shown in the parenthesis and the rest are for smaller size particles.

Here M_v is the volume of the aggregated particle, η is the viscosity of the medium (not the solution) and \bar{D} is the translational diffusion

¹) PUR stands for phenol urea condensation product. The name Syntan 25 is given for the preparation of it first in the Silver Jubilee Year (1978) of the institute (CLRI, Madras 600 020).

in the aggregated micelle. Both the aggregate rotation, equation (4a), and the translational diffusion, equation (4b), contribute to the effective correlation time T_a of the aggregate as in equation (4c). For the lateral diffusion process the radius has been chosen as the aggregated radius since the rate-limiting step in this process is expected [9] to be due to the diffusion of the polar head group.

Table 2. Various physico-chemical parameters obtained from different equations for Syntans in aqueous solution at 25 °C

System	Flory-Huggin's eqn.		Thomas eqn.		Einstein eqn.	Moulik's eqn.		Jones-Doles eqn.	
	$[\eta]$ (ml/gm)	K	V_b (ml/gm)	k_1	V_b (ml/gm)	M	K'	A	B (ml/gm)
Syntan 25	2.1	2.04	0.84	12.76	2.4	0.75	66.67	-4.416	12.86
Syntan PUR	2.9	1.98	1.16	12.40	3.3	0	150.00	-6.400	20.00

D. Hydrodynamic studies: The viscosity of various concentrated Syntans solutions were measured by Ostwald viscometer using water as the solvent medium (in case of Syntan PUR 1M urea as the solvent medium). The viscometer was calibrated using 20 per cent Sucrose solution in water and the results are more or less in good agreement with the literature value. The temperature of measurement was accurate within ± 0.1 °C. Uncertainties in temperature density measurement and the flow detection imparted a maximum error of ± 0.7 per cent to the measured viscosity.

Results and discussion

The intrinsic viscosity, $[\eta]$ has been determined using the following equation.

$$\eta_{sp}/C = [\eta] + [\eta]^2 K.C. \quad (5)$$

Here, $\eta_{sp} = \left(\frac{\eta}{\eta_0} - 1\right) =$ specific viscosity of the solution. η and η_0 are the viscosities of the solution and the solvent respectively. C is the concentration of the solution and K is the Huggins' constant. The plot of η_{sp}/C vs C has been shown in figure 1 in which the

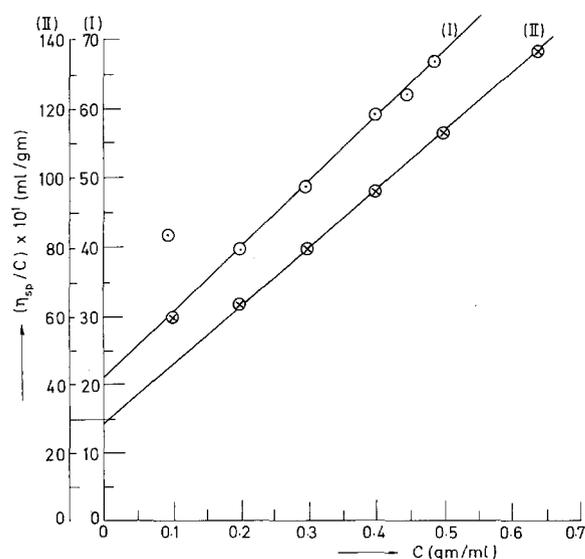


Fig. 1. Plot of η_{sp}/C vs C using Flory-Huggins equation (5) of Syntan 25 (open circle) in aqueous solution and of Syntan PUR (cross circle) in 1M Urea as the medium. Temp. = 25 °C

intrinsic viscosity $[\eta]$ and Huggins' constant, K have been calculated from the intercept and slope of the plot. Such results has been depicted in table 2. It has been observed that the values of Huggins' constant K in both Syntan 25 and Syntan PUR solution is nearly 2.0 which is consistent with the spherical shape ($K = 2.0$) of the particle although the intrinsic viscosity of Syntan PUR is approximately 1.5 times greater than that of Syntan 25. The spherical shape of the particles has also been confirmed by microscopic methods as shown in figures 2 and 3. In this regard, we mention here that if Huggins' constant, K is a diagnostic criteria for measuring the shape of the particle, then our results strongly supported in favour of spherical shape (although our results of K values are not exactly 2.0, then it may be due to some experimental deviation). Flory-Huggins equation (5) is not applicable in dilute solutions (deviation occurred at below 0.1 gm/ml, see fig. 1).

The hydrated specific volume, V_b was calculated using the following Einstein equation [10]:

$$\eta/\eta_0 = 1 + aV_b C. \quad (6)$$

In our present case, as the particles are spherical, we can safely use $a = 2.5$. The plot of η/η_0 vs concentra-

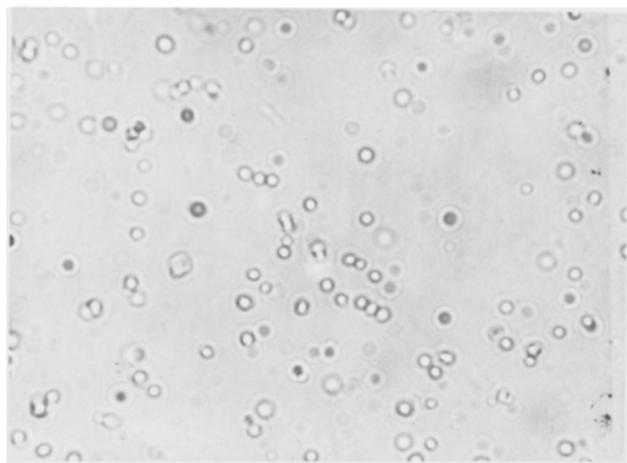


Fig. 2. The shape of the particles of Syntan 25 (0.37 gm/ml in aqueous solutions) (Magnification: X 900). Temp. = 25 °C

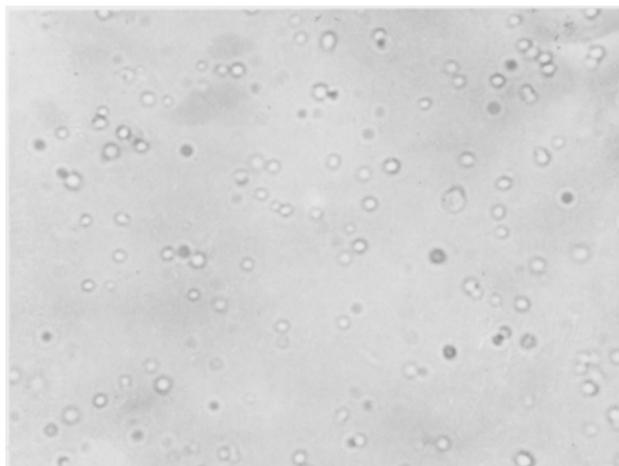


Fig. 3. The shape of the particles of Syntan PUR (0.60 gm/ml in 1M Urea as the medium) (Magnification: X 900). Temp. = 25 °C

tion has been shown in figure 4 and the calculated V_b values from that slope depicted in table 2 we have applied Moulik equation [11]

$$(\eta/\eta_0)^2 = M + K' C^2 \quad (7)$$

and the test of this equation has been shown in figure 5 and the calculated values of the Moulik' constants M and K' are given in table 2. The Moulik equation is valid for concentrated electrolyte solutions, but in our present case of Syntans although they are not electrolyte solutions, the equations (6) and (7) are valid upto concentration 0.4 gm/ml beyond which both the equations were not applicable and has been shown in figures 4 and 5 by dotted line. In table 2, we have found that the hydrated volume V_b of Syntan PUR is greater than that of Syntan 25. We have

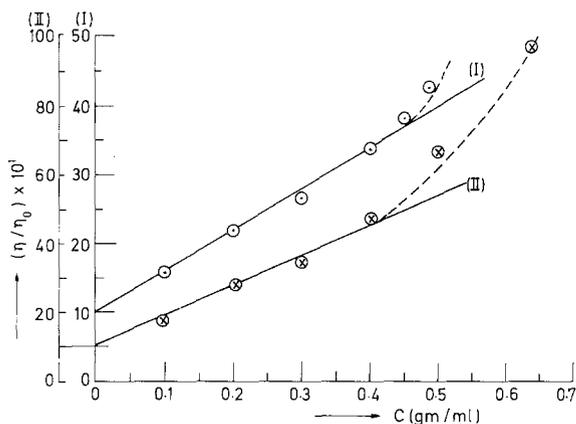


Fig. 4. Plot of η/η_0 vs C using Einstein equation (6) on Syntan 25 (open circle) in aqueous solution and on Syntan PUR (cross circle) in 1M Urea as the medium. Temp. = 25 °C

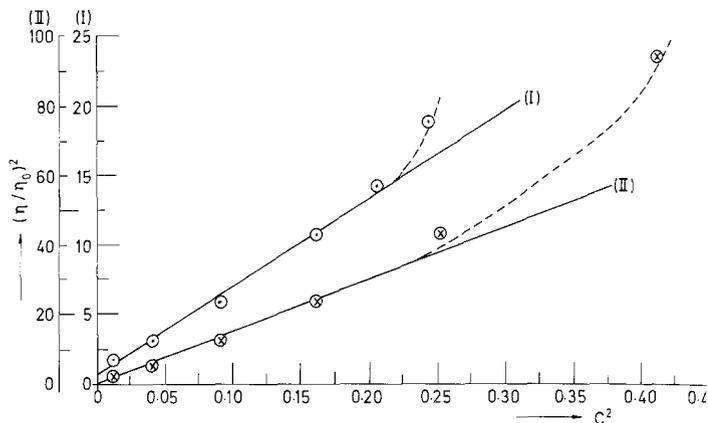


Fig. 5. Test of Moulik equation (7) on Syntan 25 (open circle) in aqueous solution and on Syntan PUR (cross circle) in 1M Urea as the medium. Temp. = 25 °C

already mentioned that Syntan PUR contained some urea (1 M Urea as the solvent medium). Now the question can be arised: whether the increase of hydration of Syntan PUR accompanies the increase of viscosity compared to Syntan 25 or the urea involved in Sytan PUR can cause the aggregated structure breaker? What does it imply? Although the confusion is unlikely, we want to solve that problem in order to enlighten the hidden phenomena happening inside the core of the aggregated structure. Well, here it is the problem! Now we turn our attention to the microscopic pictures (fig. 2 and 3). It has been found that in case of Syntan PUR, the number of aggregated particles as well as size is smaller than that of Syntan 25. Therefore, Urea contained in Syntan PUR causes a progressive reduction [12] in \bar{R}_b for the large aggregated structure. The decrease in size of the aggregated structure in case of Syntan PUR is due to the high solvation (in the present case), but the increase in viscosity apparently contradicted this view (not in the real sense). In the light of existing controversies, whether water is trapped inside the aggregated core or not, we mention here that the increase in viscosity and hydration may be possible only if water is entered in the aggregated core which can reduce the compactness of the hydrophobic group in order to enlarge (or unfurl) the structure. The special property of urea is thus invoked.

The viscosity data for different Syntans were analysed in terms of Jones-Dole equation [13].

$$(\eta/\eta_0 - 1)/C^{1/2} = A + B C^{1/2} \quad (8)$$

The plots between $(\eta/\eta_0 - 1)/C^{1/2}$ and $C^{1/2}$ are linear and has shown in figure 6. The intercept (A value) and

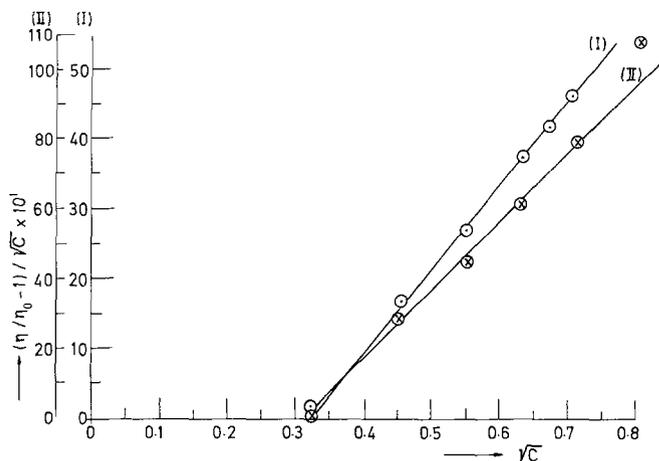


Fig. 6. Validity of Jones-Dole equation (8) on Syntan 25 (open circle) in aqueous solutions and on Syntan PUR (cross circle) in 1M Urea as the medium. Temp. = 25 °C

In figures 1, 4, 5 and 6 the curves are the corresponding ordinate scale number

the slope (B value) of the plots obtained for Syntan 25 and Syntan PUR are shown in table 2. It is clear that both the negative values of A and the positive values of B is greater in case of Syntan PUR than that of Syntan 25; which supported the contention of increasing hydration in case of Syntan PUR. Although our present systems are not strictly to be treated as a pure electrolyte (anionic system with cation as the counterion), yet the Jones-Dole equation is valid.

In terms of the concept adopted by Franks and Evans [14], the diffused layer of the anion in the Syntan PUR may be considered to consist of highly oriented water and urea molecules. The presence of urea may have caused the disruption of the so called ordering "iceberg" structure or three dimensional hydrogen-bonded "Flickering clusters" in the solvation sphere with a positive enthalpy and entropy values [2] ($\Delta H^0 = + 0.93$ Kj/mol. and $\Delta S^0 = + 8.77$ J/deg·mol. at 25 °C). Urea is a well known structure breakers of water. But it has been found that the B values increased in presence of urea (Syntan PUR) with decreasing size of the aggregated ions. This may be apparently contradicted to the hydration effect but may be attributed to the ability of these urea molecules to disrupt water structure in their vicinity.

The other various physico-chemical parameters have shown in table 1. The bigger size of the aggregated particles of Syntan 25 indicates the better filling up capacity of it with leather than of Syntan PUR. It has been shown in table 2 that the correlation times of Syntans are of the order of 10^{-5} s and this long

correlation time is due to the slow motion of aggregated micelle. This motion can consist of either the rotation of the aggregate as a single entity or the translational diffusion motion of the amphiphile along the micellar surface. The actual analysis showed that both motions take place simultaneously in series and are uncorrelated with each other and are approximately equally effective. It can be easily seen from equation (4a) and (4b) that both T_r and T_D are directly proportional to R^3 , accordingly to molecular volume M_v , of the aggregate and T_r is always greater than T_D ($T_r = \frac{4}{3} T_D$).

Since the correlation times in our present systems behave qualitatively in the same way as for other micellar systems studied [9] one might expect that the overall motion of the micellar aggregation is of importance also in these cases. The interior of the micelle is even more liquid like and it is then a reasonable assumption that the slow motion can be expected to give an important contribution to T_r and T_D (and hence to T_a) in normal hexagonal liquid crystalline phases.

Now we want to compare the following Thomas [15] equation (9)

$$\begin{aligned} (\eta/\eta_0 - 1)/C &= \eta_{sp}/C \\ &= 2.5 V_b + k_1 V_b^2 C \end{aligned} \quad (9)$$

with equation (5), we can write:

$$[\eta] = 2.5 V_b \quad (9a)$$

and

$$[\eta]^2 K = V_b^2 k_1 \quad (9b)$$

Therefore,

$$k_1 = 6.25 K \quad (9c)$$

If Huggins' constant K for spherical shape of the particle is 2.0, a phenomenon, then the value of k_1 may be 12.50 instead of 10.05 which was originally proposed by Thomas [15]. It has been reported that the value of k_1 varied from 1 to 50 depending on the nature of the system. In our present system, the value of k_1 in Syntan 25 and Syntan PUR are 12.76 and 12.40 respectively. Therefore, for spherical shape of the particles the k_1 value may be 12.50 instead of 10.05 and our contention is considered to be justified.

The Syntans really form micelles in aqueous solutions at a particular concentration (Critical micelliza-

tion concentration; cmc of Syntan 25 and Syntan-PUR are 6×10^{-3} gm/ml and 7×10^{-3} gm/ml. respectively at 25 °C) and the evidence of these micelle formation is given in our recent publication [2]. The big size of the particles of Syntans in concentrated aqueous solutions (above cmc) are due to the formation of micellar aggregation of polymeric nature. How the primary micelles of Syntans in concentrated aqueous solutions can be polymerised to form secondary micelles and so on and the details of these will be shown in our forthcoming publication.

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Received January 15, 1982;
accepted April 26, 1982

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