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Research Article

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Micellar behavior of gemini surfactant butanediyl-1,4-bis(hexadecyl hydroxyethyl methyl ammonium bromide) and its monomeric counterpart on physicochemical properties

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ABSTRACT

Measurements of physicochemical properties were carried out for understanding the behavior of mixed surfactant system containing novel hydroxylated gemini surfactant Butanediyl-1,4-bis(hexadecyl hydroxyethyl methyl ammonium bromide) 16-4-16 MEA (where MEA is monoethanol amine) and its corresponding monomeric counterpart cetyl dimethylethanol ammonium bromide (C_{16}DMEAB). The Kraft temperature (k_T), critical micelle concentration (CMC) and average degree of micelle ionization (α) of mixed micelle was determined from conductance data. CMC and α values were observed to decrease significantly with increasing mole fraction of 16-4-16 MEA surfactant in mixed micellar system. The Kraft temperature (k_T), methyl methacrylate oil (MMA) solubilization capacity, foamability and foam stability of mixed surfactant systems were also examined.

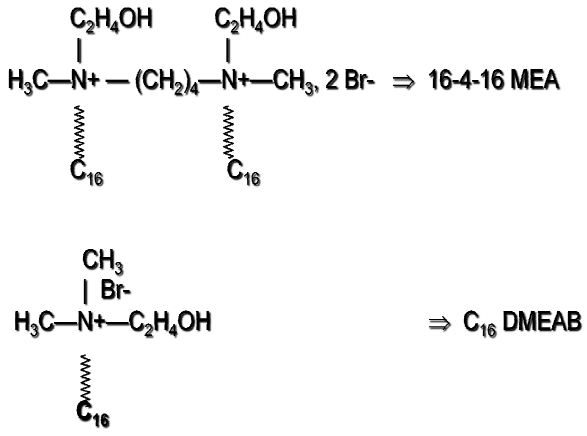
Keywords: Gemini surfactant; Head group polarity; Mixed micelle; Foamability; Oil solubilization.

INTRODUCTION

Combination of surfactants show synergistic effect in their performance as compared to single surfactant, use of mixed surfactants in industrial applications is extensively reported [1-5]. Recently gemini surfactants have attracted attention due to their unique solution properties [6-8]. These surfactants are made up of two identical amphiphilic moieties connected at the level of the head groups or at the alkyl chains but still very close to the head groups, by a spacer group which can be hydrophobic or hydrophilic, flexible or rigid [8-11]. In comparison with monomeric surfactants gemini surfactants especially with shorter spacer ($s \leq 5$) posses unusual properties, such as very low CMC, high viscoelasticity and higher aggregation tendency [11-17]. In mixed micellar system containing gemini and monomeric surfactants (16-s-16 DMA and CTAB) decrease in critical micellar concentration and increase in Kraft temperature with increase in mole fraction of gemini surfactant was reported by Zhao et al [16]. Schosseler et al [18] through SANS observed that in binary mixtures of 12-2-12 DMA and DTAB micelles progressively change from the ellipsoidal to spheroidal shapes with increase in the mole fraction of DTAB. Variation in size, shape and aggregation tendency was reported to be strongly dependent upon molecular architecture and composition of mixed surfactant systems and experimental conditions such as concentration and temperature [19-21].

Recently we have reported the effect of head group polarity of quaternary ammonium surfactants with C_{16} alkyl chain through conductance, viscosity and surface tension studies [22]. CMC values were observed to decrease when head group polarity of cationic surfactant CTAB (Cetyl Trimethyl Ammonium Bromide) increased on successive replacement of $-CH_3$ group by $-C_2H_4OH$ groups.

Hence in the present investigation we have undertaken a work of mixed micellar systems containing bis-quaternary ammonium surfactant Butanediyl-1,4-bis(hexadecyl hydroxyethyl methyl ammonium bromide) 16-4-16 MEA and its monomeric counterpart Cetyl dimethyl hydroxyethyl ammonium bromide (C_{16}DMEAB). The structures of dimeric and monomeric surfactants used in present study are given in Figure 1.



$$H_3C{-}\overset{C_2H_4OH}{\underset{C_{16}}{N^+}}{-}(CH_2)_4{-}\overset{C_2H_4OH}{\underset{C_{16}}{N^+}}{-}CH_3,\ 2\,Br^- \Rightarrow \text{16-4-16 MEA}$$

$$H_3C{-}\overset{CH_3\ Br^-}{\underset{C_{16}}{N^+}}{-}C_2H_4OH \Rightarrow C_{16}\ \text{DMEAB}$$

Figure 1. Structures of surfactants under study

EXPERIMENTAL SECTION

2.1. Materials

The novel bis-quaternary ammonium surfactant 16-4-16 MEA and their monomeric counterpart (C_{16}DMEAB) under study was synthesized and purified by well known method reported by Borse et al [23]. The purity and characterization of synthesized surfactants were checked by TLC, FTIR, ^{1}H NMR. AR grade solvents and reagents were used throughout the work. The triply distilled water was used for physicochemical measurements.

2.2. Kraft Temperature

The Kraft temperature (k_T) for the mixed surfactant system of 16-4-16 MEA and C_{16}DMEAB was determined through conductance measurements [24] as well as visual observation of the transparency of the system. Aqueous one percent (w/v) true solutions of pure and mixed surfactants were prepared and placed in refrigerator at a temperature 1 - 2^{o}C for at least 24 h, till precipitate of the hydrated surfactant crystals appeared. The precipitated system was introduced in conductivity cell and temperature of the system was gradually increased using water bath of accuracy $\pm$ 0.2^{o}C. The conductance was measured as the temperature (T) was progressively increased until the turbid solutions become transparent. The Kraft temperature was taken as the temperature where the conductance (k) versus T plot showed break and solutions were transparent. This break usually coincided with the temperature where complete dissolution of hydrated solid surfactant resulted into transparent solution. The measurements were repeated at least three times and reproducibility in Kraft temperature values was observed within $\pm$ 0.3 ^{o}C.

2.3. Conductivity

Critical micelle concentration of the mixed surfactant system was determined through conductance measurements as a function of total surfactant concentration, using Digital Conductivity Meter EQ-664 (Equiptronic, Mumbai, India) with cell constant 1.01 cm^{-1}, at 30.0$\pm$0.1^{0}C. The average degree of micelle ionization (α) and CMC were determined from specific conductance (k) verses concentration (C) plots.

2.4. Foamability and Foam Stability

Foamability and foam stability of mixed surfactant systems were studied as per the method reported by Shah and coworker [25, 26]. A graduated glass cylinder of 100 cm^3 volume was used for the measurement of the foam stability and foamability. Twenty cubic centimeters 1% (w/v) surfactant solution was poured into the calibrated cylinder. The solution was given 10 uniform jerks within 10 s. The volume of the foam generated was measured as foamability and the time required for the collapse of the foam to half of its initial hight was taken as a measure for the foam stability.

2.5. Oil Solubilisation Capacity

A mixed micellar systems containing various mole fractions of 16-4-16 MEA and its monomeric counterpart C_{16}DMEAB, at constant total surfactant concentration of 0.2 M were prepared. Solutions were thoroughly homogenized using a vortex mixter and kept in a thermostated water bath at 30 + 0.1 ^{0}C. These mixtures were then titrated with methyl methacrylate (MMA) oil using a micro-burette.

RESULTS AND DISCUSSION

3.1. Kraft Temperature

The determination of Kraft temperature through conductance measurements is superior to the commonly used method of visual observation which is dependent on the judgment of the observer. Hence Kraft temperatures (k_T) of binary mixtures of 16-4-16 MEA and C_{16}DMEAB surfactant systems were measured as a function of increased mole fraction of 16-4-16 MEA by using conductance measurement. From the Figure 2 it was observed that conductance increases rapidly with increase in temperature due to dissolution of the hydrated crystal of surfactant, until Kraft temperature reaches. Thereafter the conductance increases slowly only due to the increase in the mobility of ions with increase in temperature. The Kraft temperature determined for the mixed surfactant systems is given in Table 1. Kraft temperature was observed to increase with mole fraction of 16-4-16 MEA. This fact can be explained in terms of contributions of hydrophobic and electrostatic interactions on micellization and hence on Kraft temperature. It has been reported that increase in hydrophobicity of alkyl chain length in a surfactant molecule assists in micellization. It is also reported that increase in alkyl chain length increases Kraft temperature [27]. This means increase in micellization tendency is related to kraft temperature. If we consider electrostatic interactions which usually decrease with the addition of gemini surfactant (as α decreases, Table 2) would also assist in micellization. Therefore decrease in charge of head group facilitates micellization. Taking the analogy from the above two facts one can understand that decrease in charge should increase the kraft temperature of the system as this would increase micellization tendency as observed in the present system (Table 1).

Figure 2. (a).

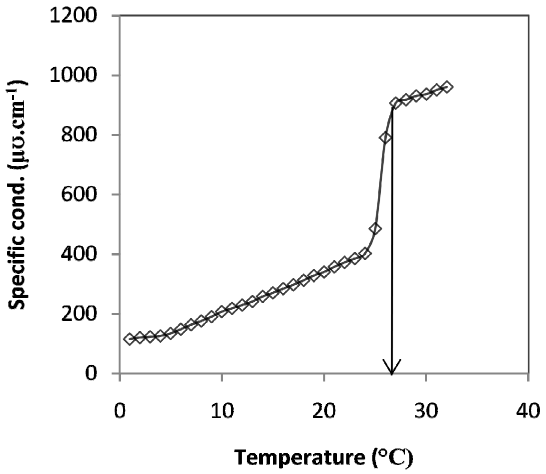


Figure 2. (b).

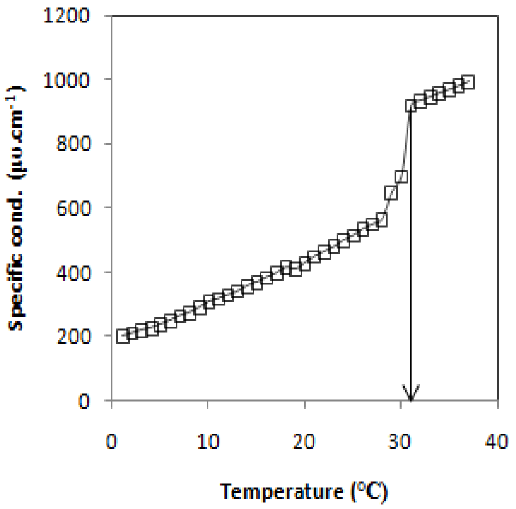


Figure 2. (c).

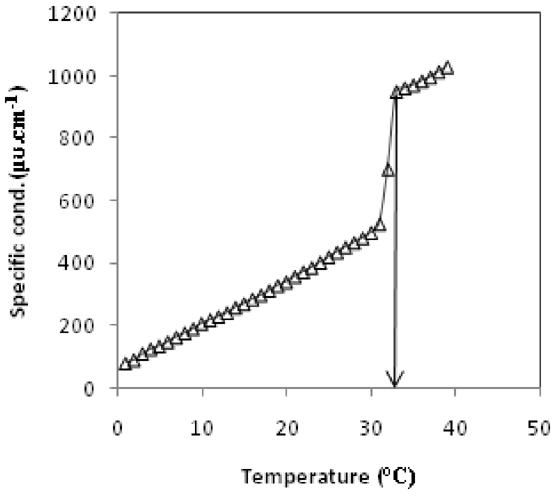


Figure 2. (d).

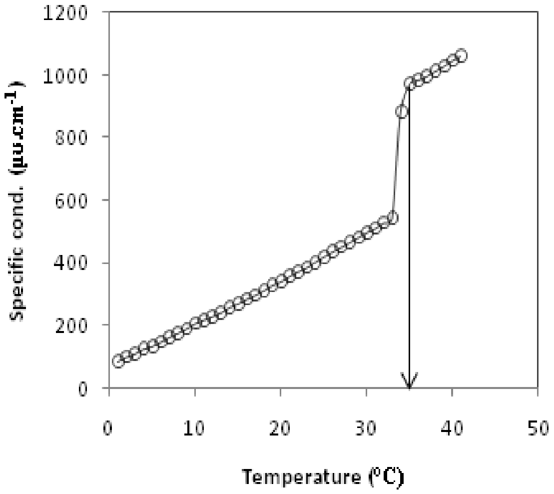


Figure 2. (e).

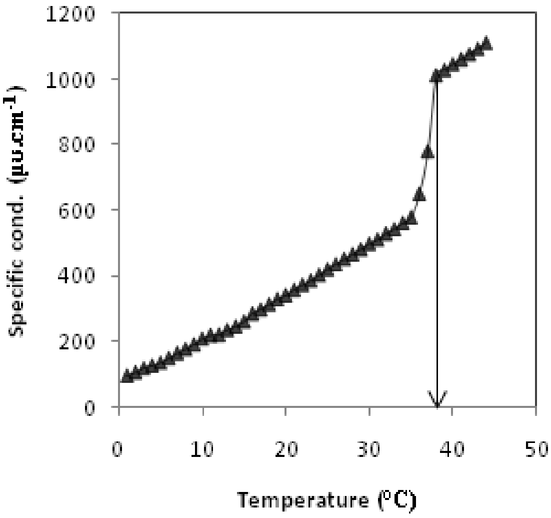


Figure 2. Plots of specific conductance against temperature for determination of Kraft temperature (k_T) of mixed surfactant system 16-4-16 MEA and C_{16}DMEAB as a function of mole fraction of 16-4-16 MEA. (a) 0.00 (◊), (b) 0.25 (□), (c) 0.50 (Δ), (d) 0.75 (O) (e) 1.00 (▲)

Table 1.Effect of mole fraction of 16-4-16 MEA surfactant on Kraft temperature (k_T) of mixed surfactant system [16-4-16 MEA + C_{16}DMEAB]

Mole fraction of 16-4-16 MEA	Kraft Temperature k_T (°C)
0.00	27
0.25	31
0.50	33
0.75	35
1.00	38

3.2. Critical Micelle Concentration

The plots for the conductometric determination of critical micelle concentrations of binary mixtures of 16-4-16 MEA and C_{16}DMEAB, as a function of mole fractions of 16-4-16 MEA (0, 0.25, 0.50, 0.75 and 1.0) are given in Figure 3. The average degree of micelle ionization (α) of the micelle was taken as the ratio of the dk/dC values above and below the CMC. The CMC, average degree of ionization micelle (α) and Gibb's free energy change of micellization (ΔG^o_m) for the mixed surfactant systems were determined from conductance data and results are given in Table 2. It was observed that CMC and α decrease with increasing mole fraction of 16-4-16 MEA in mixed surfactant system, whereas more negative value of Gibb's free energy change (ΔG^o_m) of micellization, indicates the enhancement in micellization process with increase in mol fraction of 16-4-16 MEA. Introduction of very small fraction of 16-4-16 MEA (0.25) showed drastic decrease in the CMC of mixed surfactant system. These results indicate that the 16-4-16 MEA surfactant has more tendency towards micellization than C_{16}DMEAB surfactant.

Clint equation [28] was used to determine the ideal/nonideal behavior of the mixed surfactant system by correlating the theoretical values of CMC* with experimental CMC values through the following equation.

$$1/CMC^* = x_1/c_{m1} + (1- x_1)/c_{m2} \qquad (1)$$

where x_1 is the mole fraction of the 16-4-16 MEA surfactant in the total solute concentration of mixed surfactant system and c_{m1} and c_{m2} are the respective CMC's of the pure individual surfactants 16-4-16 MEA and C_{16}DMEAB. The CMC* values for binary mixtures of 16-4-16 MEA and C_{16}DMEAB calculated using equation 1, were plotted along with experimental CMC values as illustrated in Figure 4. Good agreement between theoretically calculated and experimentally obtained CMC values was observed at particularly at higher mole fraction of gemini surfactant in the present mixed surfactant systems, indicating ideal mixing of the surfactants.

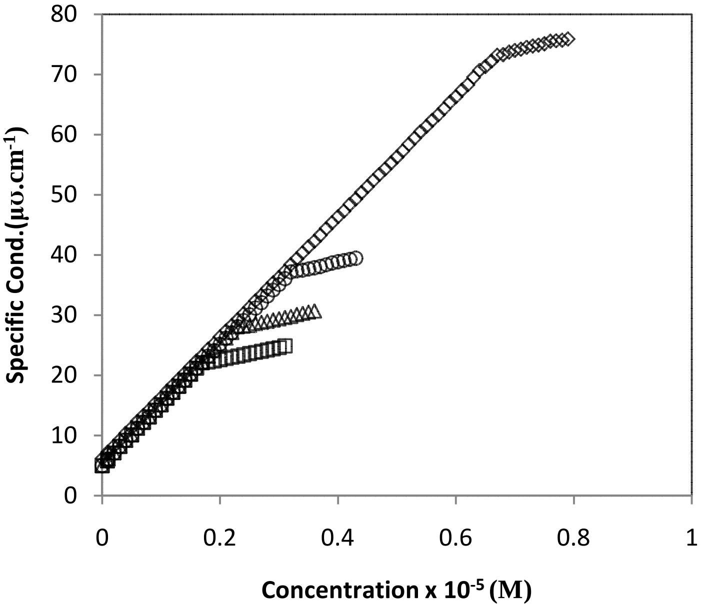


Figure 3. Plots of specific conductance (k) as a function of total surfactant concentration at 30°C and at various mole fractions of 16-4-16 MEA, 0.25 (◊), 0.50 (O), 0.75 (Δ), 1.00 (□)

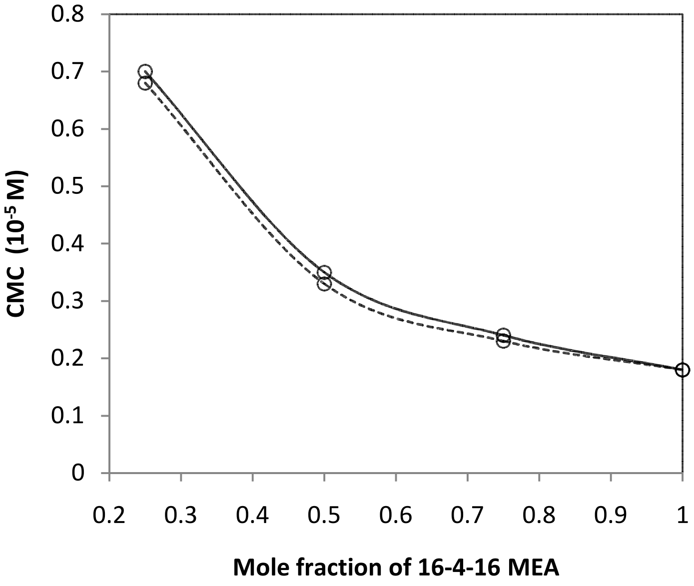


Figure 4. Plots of CMC against mole fraction of 16-4-16 MEA surfactant in binary mixture of C16DMEAB + 16-4-16 MEA at 30°C. Dotted line (Experimental CMC); Solid line (Theoretically calculated CMC*)

Table 2. Effect of mole fraction of 16-4-16 MEA on the micellar parameters of mixed surfactant systems [16-4-16 MEA + C_{16}DMEAB] at 30 ^{o}C

Mole fraction of 16-4-16 MEA	CMC (M)	CMC* (M)	Average degree of micelle ionization (α)	Gibb's Free Energy ΔG^{o}_{m} (KJ.mol^{-1})
0.00	0.21×10^{-3}	0.21×10^{-3}	0.27	-36.8
0.25	0.68×10^{-5}	0.70×10^{-5}	0.23	-53.0
0.50	0.33×10^{-5}	0.35×10^{-5}	0.22	-56.6
0.75	0.23×10^{-5}	0.24×10^{-5}	0.21	-58.5
1.00	0.18×10^{-5}	0.18×10^{-5}	0.20	-60.0

3.3. Foamability and foam stability

Foamability and foam stability as a function of mole fraction of 16-4-16 MEA in a mixed surfactant system was determined manually by the method reported by Shah [25]. The results are given in Figure 5. Foamability was observed to decrease and foam stability was observed to increase with mole fraction of 16-4-16 MEA in the mixed system. This can be attributed to the increased hydrophobicity of mixed surfactant system.

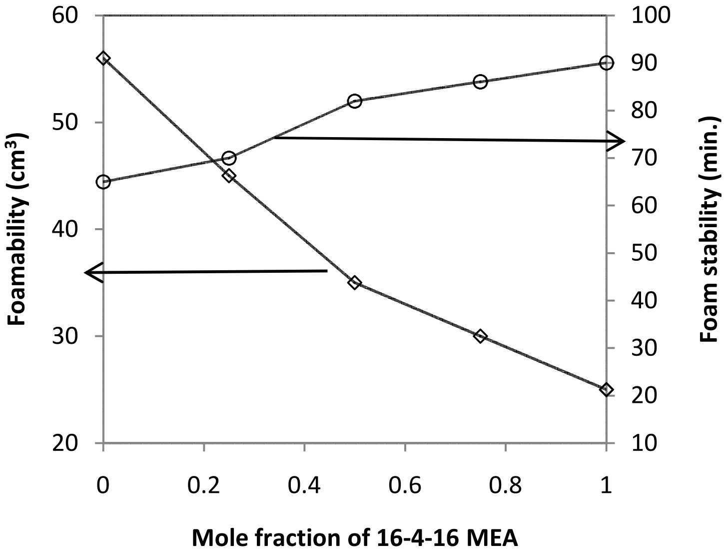


Figure 5. Foamability and foam stability as a function of mole fraction of 16-4-16 MEA for mixed surfactant system 16-4-16 MEA and C_{16}DMEAB at 0.2M and 30 ^{o}C
◊ Foamability, ○ Foam stability

3.4. Oil solubilisation capacity

Amount of methyl methacrylate (MMA) oil solubilized in a binary micellar system 16-4-16 MEA and C_{16}DMEAB against mole fraction of 16-4-14 MEA is given in Figure 6. The oil solubilisation capacity was observed to increase with increased fraction of 16-4-16 MEA in mixed micellar system. This can be attributed to the increased hydrophobicity and increased size of micelle. Shah and coworker [25, 26] reported that the oil solubilization capacity of surfactant is the important property which is related to micellar stability. Figure 6 shows that increase in oil solubilization capacity with increase of mole fraction of 16-4-16 MEA in mixed surfactant system. This can be attributed to the increased hydrophobicity and the increase in number of micelles per unit volume and increase in dimension of micelle of mixed surfactant system.

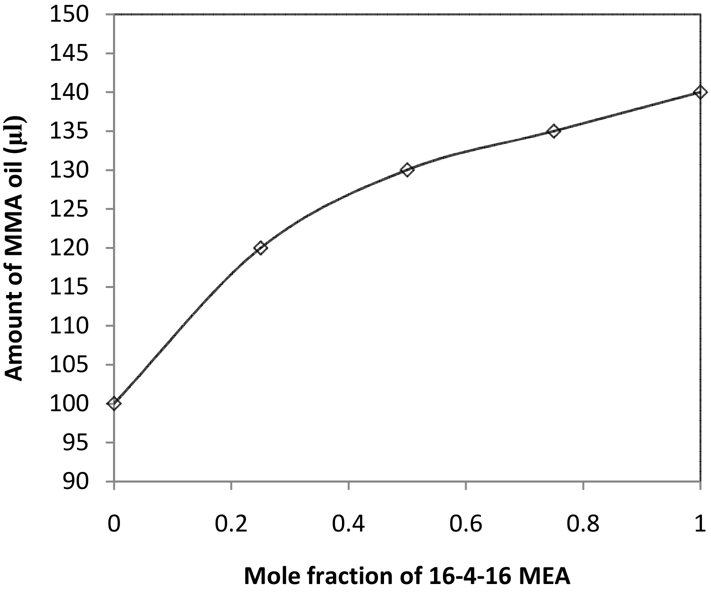


Figure 6. Effect of mole fraction of 16-4-16 MEA in binary mixture of C_{16}DMEAB and 16-4-16MEA on the solubilization of methyl methacrylate (MMA) oil at 0.2 M concentration and 30^0C

CONCLUSION

- The CMC was observed to decrease with increase in mole fraction of 16-4-16 MEA in mixed surfactant system.
- The average degree of micelle ionization decreases with increasing mole fraction of 16-4-16 MEA in mixed micellar system.
- The Kraft temperature of mixed surfactant system was observed to increase when mole fraction of 16-4-16 MEA increased.
- Foamability was observed to decrease and foam stability was observed to increase with increase in mole fraction of 16-4-16 MEA indicating increase in the stability of micelles.
- Oil solubilization capacity was also observed to increase with increase in mole fraction of 16-4-16 MEA in mixed surfactant system.

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