Studies of Binary Systems of Long Chain Alcohols

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ABSTRACT

Binary phase diagrams of some alcohols were developed and IR studies have been made in hexadecanol-octadecanol system to identify the phases. When the components differ by no more than two carbon atoms, their freezing point curves show solid solution type behavior with peaks occurring at some significant compositions. The occurrence of such peaks is considered to be indicative of molecular complex formation between the components. Alcohols mix properly with each other in their high temperature form, which is not always the case with their lower temperature modifications. The reason is attributed to the nature of the high temperature forms of alcohols. This allows effective mixing between the components to take place. IR studies are found to be quite useful in phase identification in these systems.

INTRODUCTION

The effect of water upon the polymorphism of long chain alcohols has been reported earlier (1). It then became necessary to study the effect of homologues of alcohols upon mutual polymorphism, as well as their mixing behavior in the solid state. The study of the binary system of hexadecanol and octadecanol, particularly, became important from a different point of view as well. Hexadecanol is used to suppress water evaporation from reservoirs, and it has been observed that the efficiency of spreading hexadecanol on the water surface increases if the latter is mixed with a little octadecanol (2). It also has been noticed that the β-crystal form of alcohols has greater spreading properties than the γ-modification.

The work reported here includes the study of the binary systems of alcohols of even and odd carbon numbers of different chain length. IR study was applied to identify the various phases in the hexadecanol-octadecanol system.

MATERIAL AND METHODS

Fluka Purissimum dodecanol was distilled twice under reduced pressure over quicklime. The fraction boiling between 95 C and 96 C under 0.9 mm pressure was used. Hexadecanol was Fluka Purissimum grade distilling between 122-124 C under 0.8 mm pressure. Fluka Purissimum octadecanol distilling between 145-146 C under 0.35 mm pressure was used. Tridecanol was Koch-Light pure grade; the fraction boiling between 109-110 C under 0.2 mm pressure was used. Pentadecanol was also Koch-Light pure grade, and the fraction boiling between 137-138 C under 0.8 mm pressure was used. All the distillations were performed using an efficient fractionating column, and gas liquid chromatography on all the materials showed that none had more than 1% impurity. The samples were prepared by adding differing amounts of one component into the other. The components were mixed on melting. The freezing and transition points were obtained from time-temperature curves recorded by using a well calibrated chromel-alumel thermocouple connected through a direct current amplifier to a potentiometric recorder (3).

The reproducibility of both freezing and transition points was within 0.3 C. The samples were cooled at the rate of ca. 0.3 C/min, and the time temperature curves showed well defined breaks at the freezing and transition points. A Grubb-Parsons Spectromaster prism-grating

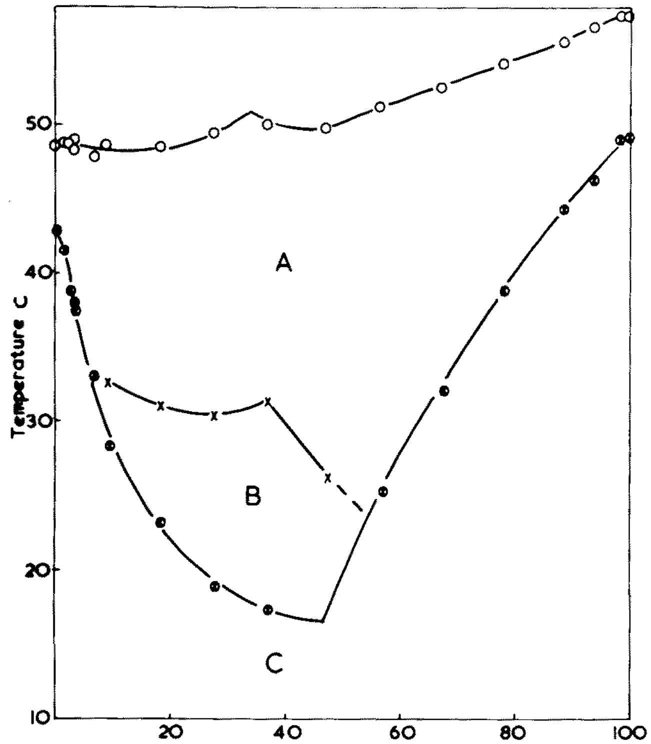

FIG. 1. Phase diagram of hexadecanol-octadecanol system. O = freezing points and X and ⊗ = transition points.

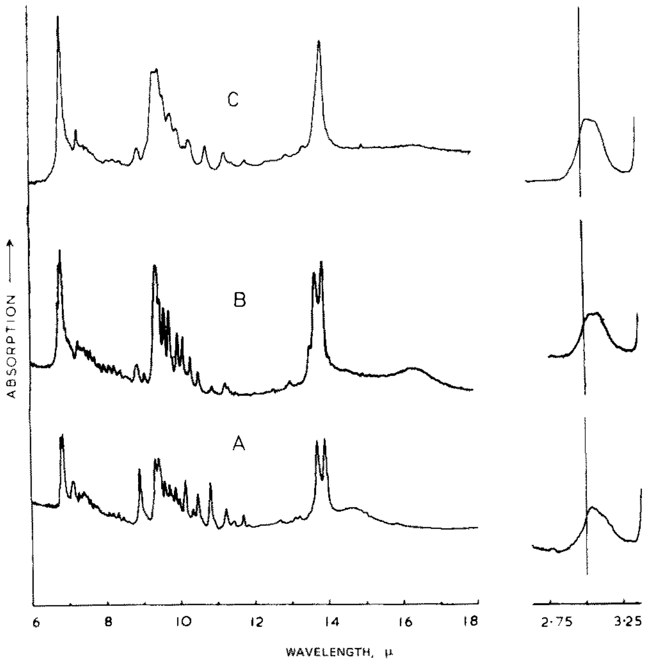

FIG. 2. IR spectra of different polymorphic forms of long chain alcohols. A = heptadecanol in the β-form, B = hexadecanol in the γ-form, and C = tetradecanol in the α-form.

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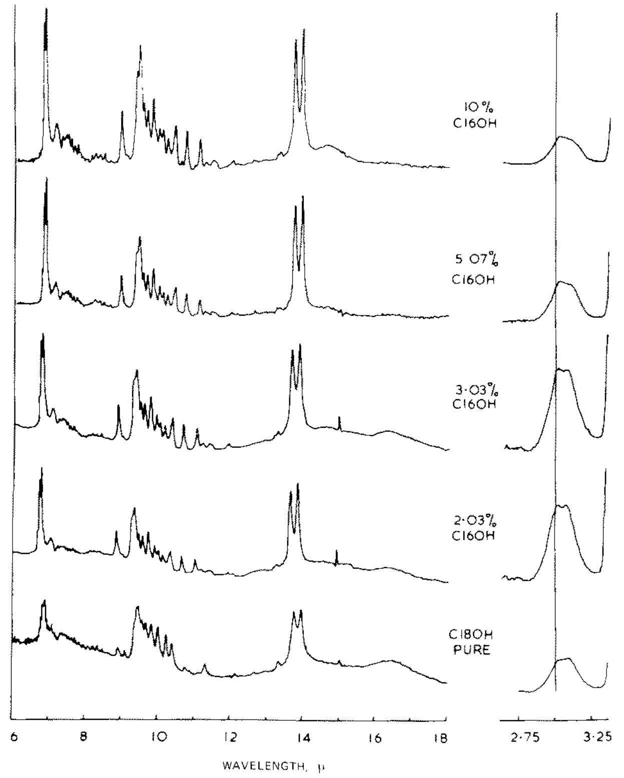

FIG. 3A. IR spectra showing the effect of variable amount of hexadecanol upon the polymorphism of octadecanol.

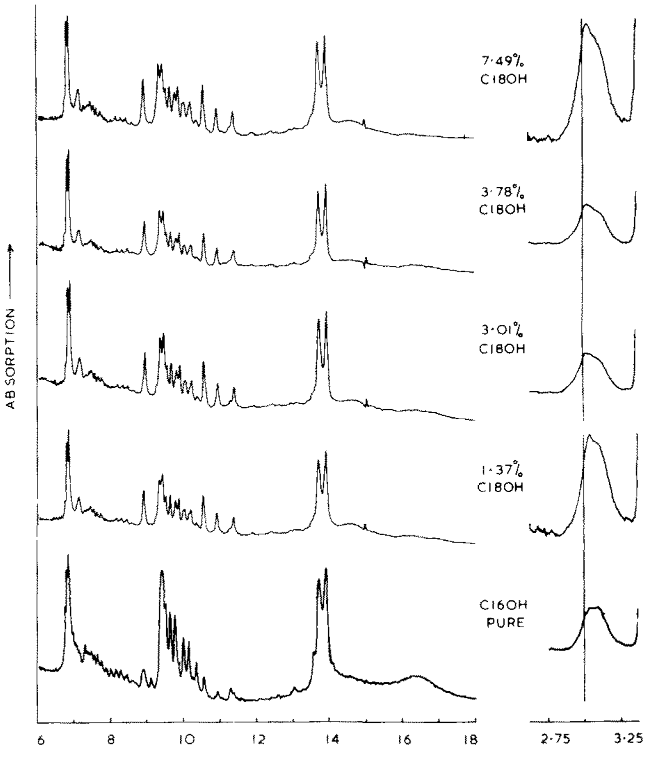

FIG. 3B. IR spectra showing the effects of variable amount of octadecanol upon the polymorphism of hexadecanol.

monochromator equipped high resolution IR spectrometer was used to record the IR spectra. For recording the spectra above room temperature, a variable temperature cell was used.

RESULTS AND DISCUSSION

Hexadecanol-Octadecanol System

The phase diagram of the hexadecanol-octadecanol system is shown in Figure 1. The freezing points fall on a solid solution curve with a very small peak at 34% hexadecanol. As the percentage of one of the components in the other increases, the cooling curves show gradual changes, the definiteness of the freezing point flat is lost, and the substance freezes over a temperature range. The samples containing 6.53-47.4% octadecanol show 2 transitions in the solid state, the lower temperature break being longer than the higher. With increased amount of octadecanol, the super cooling that used to occur near the transition point of pure hexadecanol diminishes and completely disappears at higher concentrations of octadecanol. The lower transition temperature break also becomes smaller and smaller with a greater amount of octadecanol and finally becomes undetectable in the 47.4% octadecanol sample. The other side of the phase diagram is similar, though only one solid transition break is obtained. Because of two solid state transitions occurring close to the hexadecanol side of the phase diagram, a small phase region denoted by B was created. The depression of the transition point of hexadecanol by octadecanol is more marked than that for octadecanol by hexadecanol; but, as can be seen from the phase diagram, below 3% octadecanol, there is comparatively less depression of transition point than at higher concentration of octadecanol. On the other hand, from the octadecanol side, the depression of the transition point is nearly uniform throughout. No lower temperature transition could be detected in the 47.4% octadecanol sample, and extrapolation of two transition point curves resulted in a shallow eutectic at 49.2% of octadecanol.

Three representative spectra of β,γ, and α forms of alcohols are shown in Figure 2 in which heptadecanol ($C_{17}OH$) shows the characteristic β-form spectra and hexadecanol ($C_{16}OH$) the γ-form spectra. Both β and γ forms of alcohols give α-form specta 1 and 2 C before melting. The spectral characteristics of β-form crystals of alcohols are as follows: (A) noticeable intense OH bending (in-plane) band at ca. 7.1μ, (B) complexity of the absorptions between 7.14-8.7μ, (C) reasonably strong band at 8.9μ, (D) occurrence of OH bending (out-of-plane) band at ca. 14.6μ, (E) OH stretching vibration band occurring with a low frequency shoulder, and (F) strong bands in the region 10.5-11.8μ.

The spectral characteristics of the γ-form crystals are: (A) OH bending (in-plane) band occurring at ca. 7.03μ with extremely low intensity, (B) simplicity of the bands in the region 7.14-8.7μ, (C) weak intensity of the band at ca. 8.9μ, (D) occurrence of the OH bending (out-of-plane) band at ca. 16.3μ, (E) OH stretching vibration band occurring as a doublet, and (F) weak instensity of the bands in the region 10.5-11.8μ.

The α-form spectra are characterized by the following: (A) singlets at 6.75μ and 13.75μ arising from CH_2 bending and CH_2 rocking vibrations, respectively (in low temperature modifications of alcohols, both these bands are doublets), (B) simplifcation and reduction in intensities of most of the bands between 7-13.5μ, and (C) intensity increase, simplification, and lower wave length shift of OH stretching vibration band near 3μ.

Figures 3A and 3B show the spectra of the binary system of hexadecanol-octadecanol within limited concentration (10%) of each component. It can be seen from the spectra that less octadecanol is required to convert hexadecanol into the β-phase than hexadecanol to do the same to octadecanol. Figure 4 shows the spectra of the 29.98 mole percent octadecanol sample at 8 C and at 25 C and also the spectra of the 49.9 mole percent octadecanol sample at 40 C. The 29.98 mole percent octadecanol sample at 8 C lies below the freezing and transition points, and the spectra

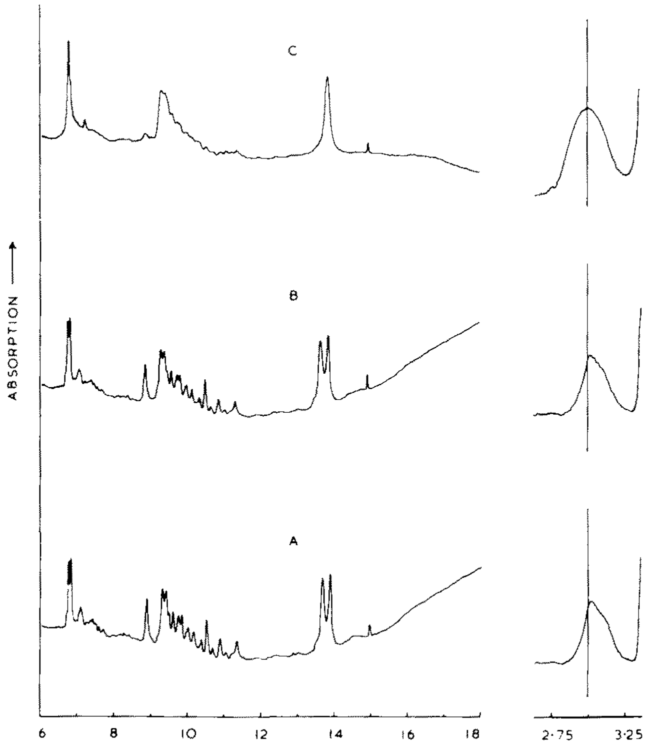

FIG. 4. IR spectra of hexadecanol-octadecanol system. A - 29.98 mole percent octadecanol at 8 C, B = 29.98 mole percent octadecanol at 25 C, and C = 49.9 mole percent octadecanol at 40 C.

show that the sample was in the β-form at this temperature. The same sample at 25 C exists in a phase which is denoted by B in the phase diagram. The spectrum at this temperature also shows that the sample was in the β-form. The 49.9 mole percent octadecanol sample at 40 C exists in a phase which is denoted by A in the phase diagram. Spectra show that the sample was in the α-form at this temperature.

Pentadecanol-Hexadecanol System

Figure 5 shows the phase diagram of pentadecanol-hexadecanol. The freezing points give a solid solution type curve with a small peak at ca. 50 mole percent. Between 17.55-59.15% hexadecanol, the cooling curves show 2 breaks in the solid state, implying 2 transitions. As a result of this, the phase area denoted by B was produced. The lower transition points fell on a fairly smooth curve showing a minimum at ca. 30% hexadecanol.

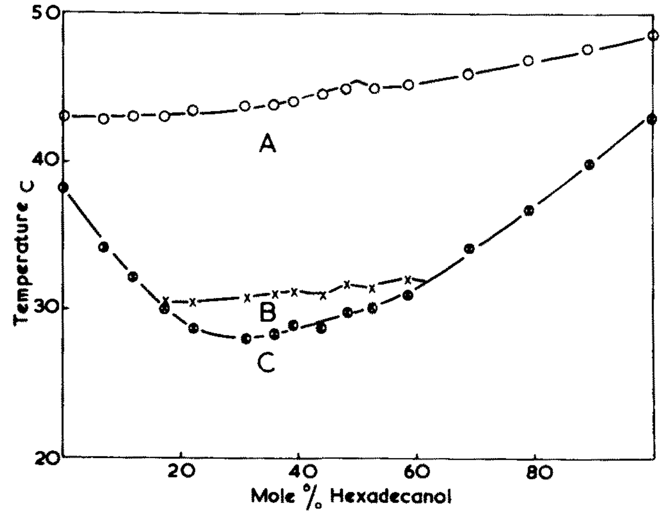

FIG. 5. Phase diagram of pentadecanol-hexadecanol system. O = freezing points andX and⊗= transition points.

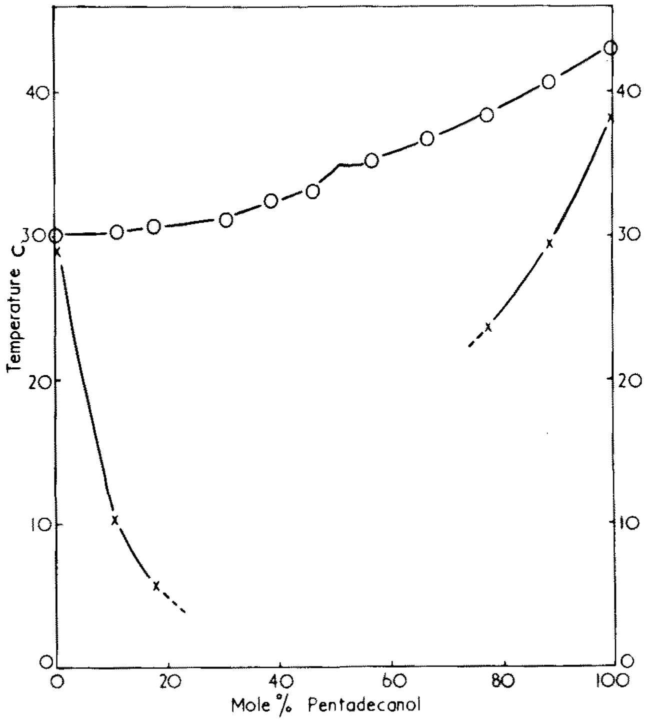

FIG. 6. Phase diagram of tridecanol – pentadecanol system. O = freezing points and X = transition points.

Tridecanol-Pentadecanol System

The phase diagram of the system is presented in Figure 6. The freezing points give a solid solution type of curve with a small peak at ca. 50%. Greater depression of transition point of tridecanol is produced by pentadecanol rather than pentadecanol by tridecanol. The samples between 31.4-67.7% pentadecanol do not show any transition in the solid state.

Dodecanol-Octadecanol System

Figure 7 shows the phase diagram of dodecanol-octadecanol. The freezing point curves form an eutectic at 12% octadecanol. The transition point of dodecanol is lowered by the addition of up to 86% octadecanol; above this, the solid state transition disappears. The intersection of freezing and transition point curves of dodecanol occurs at ca. 5% octadecanol. This behavior of intersection of freezing and transition point curves of dodecanol is similar to that observed in dodecanol-water system in which the intersection occurs at ca. 0.5% water (1). The transition point of octadecanol, on the other hand, is not lowered by dodecanol. As a result, the transition point curve meets the freezing point curve at ca. 68% octadecanol. Due to this, a triangular α-phase area was created close to the octadecanol axis.

The freezing point curves of all the binary systems of alcohols studied, except the dodecanol-octadecanol system, show occurrence of peaks which may be significant. Such peaks existing in solid solution type curves of these alcohols are not observed in other binary systems of amphiphilic substances. Carey and Smith (4) obtained similar peaks in the solid curves of the binary system of odd and even alcohols. But as can be seen from the results presented here, such peaks commonly occur in the binary freezing point curves of alcohols when the components do not differ from each other by more than two carbon atoms in the chain. In the hexadecanol-octadecanol system, this peak occurs at a composition which corresponds to one molecule of hexadecanol to two molecules of octadecanol. In the phase diagrams of the binary systems of pentadecanol-hexadecanol and tridecanol-pentadecanol, these peaks occur nearly at equimolar compositions. The position of the peaks in hexadecanol-octadecanol, pentadecanol-hexadecanol, and tridecanol-pentadecanol systems correspond to 51 C, 45.4 C, and 34.8 C, respectively. The occurrence of such peaks indicates that the two components form some sort of molecular complex at the compositions corresponding to the peaks. The situation is similar to well known iodine-bromine systems. The solid solution type of curve at the freezing pooint illustrates the easy miscibility of the two components in their high temperature form. This is quite expected in view of the structural similarity of the high temperature form of odd and even alcohols. In this form, the molecules are vertical to their end-group plane, hexagonally arranged in some sort of rotational movement. In such a phase, the mixing of the components will be greatly favored, resulting in the solid solution type of curve at the freezing point. Benton (2) suggested a new α-form (termed α′ by him) in 90% hexadecanol-10% octadecanol and also in the equimolar mixture of the two. This might be the α-form of the solid solution and of the molecular complex of hexadecanol and octadecanol. In these cases, the α-form could have a little different structure from the α-form of pure compounds. The IR spectra of Figures 3a and 3b show the change in the room temperature polymorphic form of hexadecanol produced by variable amounts of octadecanol and vice versa. The spectra can be utilized to determine compositions of the samples depending upon intensities of some of the bands used for phase identification. The spectra also show the minimum amount of octadecanol needed to transform hexadecanol into β-phase which is important in the use of hexadecanol as antievaporant of water from reservoirs. Since the IR spectra show that octadecanol is relatively more effective to produce change in the hexadecanol lattice, they provide an explanation to the difference in slope of the transition point curves in the phase diagram of hexadecanol-octadecanol system.

The formation of eutectic by the transition point curves in hexadecanol-octadecanol system indicates less tendency for mixing of the low temperature crystal forms of the two components. Though both the alcohols are changed from γ into β-forms by each other, the β forms of the two may be structurally different.

The wide difference of chain length between dodecanol and octadecanol seems to be responsible for the formation of eutectic in the freezing point curve. Octadecanol noticeably lowers the transition point of dodecanol, but dodecanol apparently produces no effect upon the transition point of octadecanol. This shows that the lattice of octadecanol is virtually ineffective to the presence of dodecanol, because they cannot properly mix, which is reflected in the eutectic type of behavior of their freezing point curve. A one carbon atom difference between pentadecanol and hexadecanol results in the smooth transition point curve which is indicative of better mixing between their low temperature crystal forms.

Wherever a third arrest of temperature occurred in the cooling curves of these systems, the second arrest was always much shorter lived than the first and the third. These second arrests of temperatures in these systems might, in general, correspond to the transformations of some metastable phases.

The complete disappearance of solid state transition from the samples containing 31.4-67.7% pentadecanol in tridecanol-pentadecanol system suggests that a different type of crystal is obtained on mixing the components in these proportions.

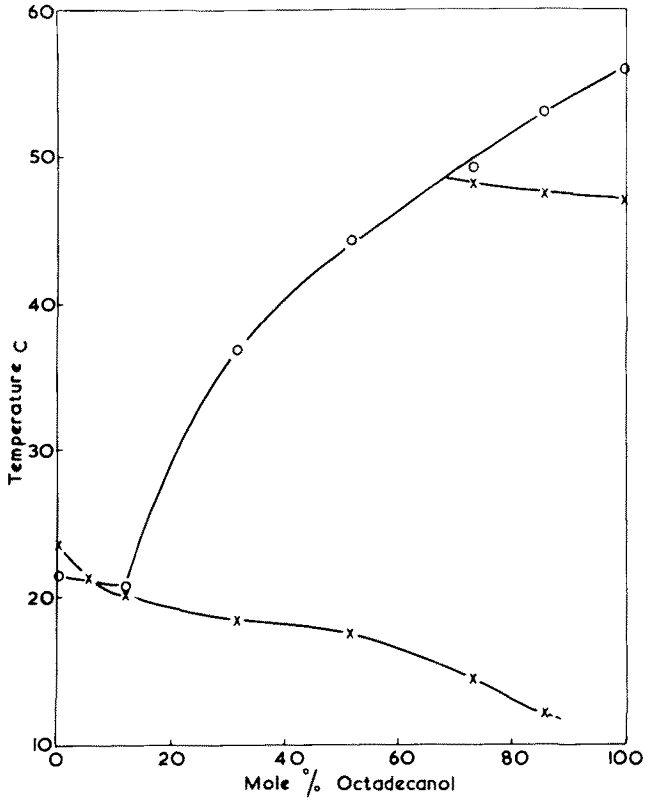

FIG. 7. Phase diagram of dodecanol-octadecanol system. O = freezing points and X = transition points.

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