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Article

Charge Transfer Complexes Between Indole Derivatives and Methyl Viologen in Normal and Reverse Micellar Systems

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A interação de transferência de carga entre metilviologênio (MV^{2+}) e triptofano (Trp), ácido indolacético (IAA) e ácido indolbutírico (IBA) foi estudada em água, em soluções aquosas de dodecilsulfato de sódio (SDS), de cloreto de cetiltrimetilamônio (CTAC) e em micelas invertidas de bis(2-etilhexil)sulfosuccinato de sódio (AOT) em heptano. As constantes de associação aparentes foram determinadas. Na presença de SDS ou de CTAC, os valores são da mesma ordem de grandeza que em água, mas eles dependem da concentração de surfactante. Em AOT, os valores da constante de equilíbrio de IAA e Trp são muito maiores que em água e mostram uma forte dependência da relação água/surfactante (*R*). Os valores de IBA são muito inferiores, similares aqueles obtidos em água e praticamente independentes de R. Estes efeitos podem ser explicados considerando a participação dos componentes entre as diferentes microfases. Fotólise a laser do complexo produz o cátion-radical do metilviologênio em baixo rendimento apenas no caso das soluções de CATC, em que o processo de separação de cargas é favorecido.

The charge transfer interaction between methyl viologen (MV^{+2}) and tryptophan (Trp), indole acetic acid (IAA) and indole butyric acid (IBA) was studied in water, in aqueous solutions of sodium dodecyl sulfate (SDS), cetyltrimethylammonium chloride (CTAC) and in reverse micelles of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) in heptane. The apparent association constants were determined. In the presence of SDS or CTAC the values are of the same order of magnitude as in water, but they depend upon the surfactant concentration. In AOT the values of the equilibrium constant for IAA and Trp are very much higher than in water and they show a strong dependence upon the water/surfactant ratio (*R*). For IBA the values are much lower, similar to those in water and show practically no variation with *R*. These effects may be explained by considering the partitioning of the components between the different microphases. Laser flash photolysis of the complex produces the radical cation of methyl viologen in low yield only in the case of CTAC solutions where the process of charge separation is favoured.

Keywords: *indole derivatives, micellar systems*

Introduction

It is well known that the methyl viologen (Paraquat dichloride, 1,1'-dimethyl-4,4'-bipyridinium dichloride, $(MV^{+2})(Cl^{-})_2$) forms ground-state, electron-donor acceptor (EDA) complexes with a variety of electron donors [1,2]. Most of these studies were carried out in homogeneous solutions. It is also of interest to investigate the effect of organized systems on the properties of these complexes. Several papers have been published on the effect of surfactants on EDA complexes formed by methyl viologen with different donors. In the case of naphthylamines[3] in the presence of sodium dodecyl sulfate (SDS) the observed association constants with MV^{+2} were much higher than in the absence of the detergent, but they were strongly dependent upon the SDS concentration. The EDA complexes of MV^{+2} with other naphthalene derivatives[4] acting as electron donors were also studied in SDS. Pyrene and methylviologen in the presence of SDS micelles form an EDA complex characterized by the presence of a new band in the visible spectrum[5,6]. This complex was also investigated by fluo-

rescence quenching techniques[7]. In practically all cases when surfactant effects were studied, normal micelles were formed. The formation of EDA complexes in reverse micellar solutions received very much less attention.

The particular case of the interaction between methylviologen and indole and its derivatives deserved special attention because of the relevance of these complexes in relation to biological systems[8]. From this point of view it is of special concern to investigate the effect of organized systems such as micelles, reversed micelles and polyelectrolytes, on the complexes formed by these molecules. The interaction of indole and tryptophan with normal[9] and reverse micelles is well documented, and it is known that MV^{+2} strongly associates with SDS micelles[3]. In an early study Martens and Verhoeven[5] showed that the complex formation between indole and MV^{+2} is favored in SDS micelles. This was confirmed later by Park and Hwang[10] in a study of the effect of SDS and polyelectrolytes on the charge transfer interaction of indole derivatives with MV^{+2}. It was observed that the negative polyions also enhanced the complex formation of neutral indole and zwitterionic tryptophan with MV^{+2} while the presence of SDS produces a similar but larger effect. Later an experimental and theoretical study was published of the effect of polyelectrolytes on the association constants of the complexes between alkylviologens and indole derivatives[11]. The results were explained by a model that considers hydrophobic interactions as well as electrostatic forces in the formation of the EDA complexes.

To our knowledge the effect of reversed micelles on the EDA complexes of MV^{+2} with indole and its derivatives has not been reported in the literature. Reverse micelles may be considered as a very primitive model of biological systems. They provide three different sites for the solubilization of small molecules; the interface formed by the polar head of the surfactant molecules, the water pool and the bulk organic phase. It is therefore of interest to investigate the formation of MV^{+2}-indole complexes in these systems. To this end the available information about the distribution of indole and derivatives in AOT (sodium dioctyl sulfosuccinate) - heptane reverse micelles[12] is very useful. The partitioning of MV^{+2} in AOT reverse micelles was also reported[13]. With this information at hand we undertook an investigation of the formation of EDA complexes between MV^{+2} and indoles in AOT/heptane reverse micelles. In this paper we present results on these systems together with a similar study in normal micelles. In spite of the considerable amount of work published in homogeneous solution and micellar solution, the effect of the sign of the charged interface in normal micelles, and the structure of the indole derivatives was not, to our knowledge, systematically investigated. Here we present a study of the effect of anionic (SDS) and cationic (CTAC, cetyltrimethylammonium chloride) micelles on the association of tryptophan, indole-3-acetic acid, and indole-3-butyric acid with MV^{+2}.

Also, we include in this paper a preliminary investigation of the photochemistry of these EDA complexes. Such studies have received considerable attention during recent years[14]. It is well known that in some cases the photolysis of EDA complexes may lead to the formation of free radical ions. This charge separation process was investigated by picosecond and nanosecond flash photolysis[15]. The formation of the MV^{+2} radical cation was also observed upon irradiation of several complexes of MV^{+2} (for a review see Ref. 14). Also the photochemistry of the naphthalene derivatives - MV^{+2} complexes was studied in water and in micellar solutions[4]. Here we show some results pertaining to the charge separation efficiency after laser pulse excitation of the indole derivativesMV^{+2} complexes.

Experimental

L-Tryptophan (Trp) (Sigma), indole-3-acetic acid (IAA) (Koch Light) and indole-3-butyric acid (IBA) (Sigma) were used without further purification. Methyl viologen dichloride $(MV^{+2})(Cl^{-})_2$ (Aldrich) and tris[hydroxymethyl]-aminomethane (Tris) (Aldrich) were used without further purification. Cetyltrimethylammonium chloride (CTAC) and sodium dodecylsulfate (SDS) were recrystallized from commercial products by standard procedures. Dioctyl sulfosuccinate, sodium salt (AOT) (Sigma) was used as received. n-Heptane (Sintorgan) HPLC grade and triply distilled water were employed. UV-vis absorption spectra were recorded with a Hewlett Packard 8452A diode array spectrophotometer. All measurements were carried out at 20 ± 1 °C.

The association constants of MV^{+2} with the indole derivatives were determined by following the change in the absorbance of the charge-transfer band produced by changing the MV^{+2} concentration at fixed indole concentration. The absorbance at the maximum of the band (λ_{max}) was determined by subtracting the absorbance of solutions containing the same concentration of MV^{+2} and surfactant. The plots of absorbance *vs.* $[MV^{+2}]$ were fitted by a non-linear least squares procedure to a 1:1 equilibrium with the equilibrium constant K_{as}, and the extinction coefficient ε, as adjustable parameters. The values of K_{as} and ε were obtained by an iterative procedure previously described. In the studies of homogeneous solutions and normal micelles the concentration of MV^{+2} was varied between 2×10^{-4} and 2×10^{-2} M. The concentrations of SDS and CTAC were also changed between 1×10^{-4} and 5×10^{-2} M. Indole derivatives were kept fixed at 1×10^{-2} M. All the solutions were made in 0.01 M Tris. The association in AOT reverse micelles was studied at fixed surfactant concentration (0.2 M). The size of the water pool was varied by addition of water with 0.01 M Tris. The ratio R = [water]/[surfactant]

was varied from 5 to 25. In the reverse micelles study the concentration of the indole derivatives was 1 x 10^{-4} M.

For laser flash photolysis experiments either a nitrogen laser (Laser Optics, 7 ns FWHM and 5 mJ per pulse) or a frequency tripled Nd-YAG laser (Spectron Lasers) for irradiation at 355 nm were employed. The signal from the PM tube was acquired by a digitizing scope, averaged and then transferred to a computer. Quantum yields of $MV^{+\cdot}$ were determined by actinometry with ZnTPP (zinc tetraphenyl porphyrin) in benzene as previously described[17]. The triplet yield of ZnTPP was measured at 470 nm immediately after the laser pulse. All measurements were performed in deaerated solutions at 298 K.

Results and Discussion

Normal micelles

The EDA complexes formed by indolic compounds and MV^{+2} are characterized by a broad charge-transfer band centered around 400 nm. Figures 1 and 2 show the absorption spectra of these complexes for Trp in water at pH 8, and in the presence of variable concentrations of CTAC and SDS, respectively. The apparent association constant K_{as}, and the molar extinction coefficients of the complexes in water in the absence of surfactants, are collected in Table 1. The corresponding quantities previously reported in the literature are also included in the table for the sake of comparison. It can be seen that the results show some variation which is typical for this type of measurement. This variation is most probably due to different experimental conditions and to the treatment of experimental data. Our values, although not coincident, are similar in magnitude to those of other sources. It can be seen that the association constants are very similar for the three indole derivatives in water. The slightly higher values for IAA and IBA compared with Trp reflect the influence of the net negative charge of the molecule. It was reported[2] that indole itself also forms an EDA complex with MV^{+2} in EtOH with an association constant of 8.20 M^{-1}.

The λ_{max} and spectral width of the charge transfer band remain unchanged in the presence of SDS and CTAC. However, as can be observed in Fig. 1 for MV^{+2} and Trp, the intensity decreases when the CTAC concentration increases while an opposite effect is observed in the presence of SDS (Fig. 2). The association constants depend on the surfactant concentration and Fig. 3 shows K_{as} for IAA, IBA and Trp as a function of CTAC concentration. It can be seen that the values decrease when the surfactant concentration increases beyond the cmc (critical micellar concentration = 1.4 x 10^{-3} M for CTAC in pure water). This may be understood by the association of the indolic compounds with the micelles. Since MV^{+2} may be considered to remain unassociated due to the electrostatic repulsion, the association of the negatively charged IAA and IBA with the micelles produces the observed reduction. Also Trp is known to associate with CTAC micelles[9] and the same explanation is valid in this case. The increase in K_{as} observed for IAA in the premicellar region is not easily explained, but it may be due to a specific salt effect[19].

Table 1. Spectral parameters and association constants of EDA complexes of indolic compounds with methylviologen in water pH 8.

Indole	λ_{max} /nm	ε / $M^{-1}cm^{-1}$	K_{as} / L mol^{-1}
Tryptophan	400	275[a]	16[a]
IAA	396	245[a], 660[b], 422[c]	22[a], 13.5[b], 47[c]
IBA	398	280[a], 640[b]	24[a], 14.7[b]

[a] this work, [b] Ref. , [c] Ref.

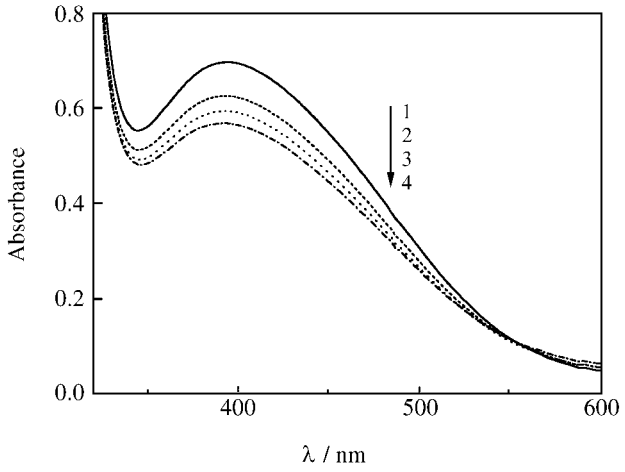

Figure 1. Absorption spectra of tryptophan 1 x 10^{-2} M, MV^{+2} 2 x 10^{-2} M in water at variable concentration of CTAC (pH 8). (1) [CTAC] = 0 M, (2) [CTAC] = 9.9 x 10^{-3} M; (3) [CTAC] = 2 x 10^{2} M, (4) [CTAC] = 3 x 10^{2} M.

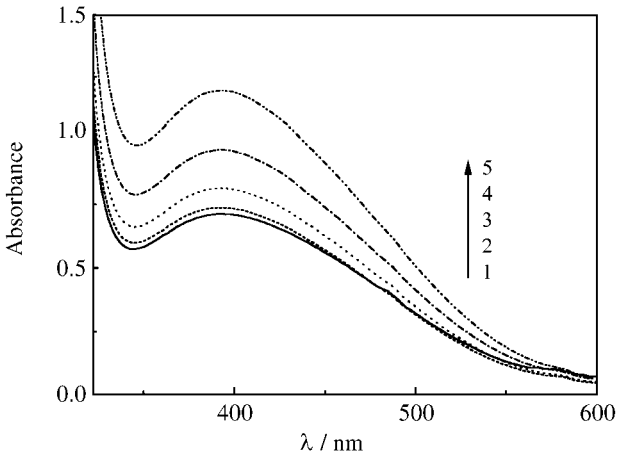

Figure 2. Absorption spectra of tryptophan 1 x 10^{-2} M, MV^{+2} 2 x 10^{-2} M at variable concentrations of SDS (pH8). (1) [SDS] = 0, (2) [SDS] = 2.4 x 10^{-3} M, (3) [SDS] = 4.8 x 10^{3} M, (4) [SDS] = 9.9 x 10^{-3} M, (5) [SDS] = 2 x 10^{-2} M.

Figure 4 shows the dependence of the association constants with SDS concentration. For IAA and IBA they diminish in the presence of the surfactant. This can be understood by considering that the IAA or IBA anions are repelled from the negatively charged interface, while MV^{+2} strongly associates with the detergent[3], lowering also the cmc with respect to its value in pure water. For this reason the results can not be explained taking into account only a simple ionic-strength effect because MV^{+2} induces the micellization process at lower concentration than in water and then the most important effect is related with the presence of the micelles, even at the lowest SDS concentration. The opposite effect, an increment of the association constants values**,** is observed in the case of Trp. This may be rationalized by considering that the aminoacid associates with the SDS micelles as previously reported[9]. In this way, since MV^{+2} local concentration is greatly increased at the micellar interface, the apparent association constant is higher due to a local concentration effect in the micellar pseudophase.

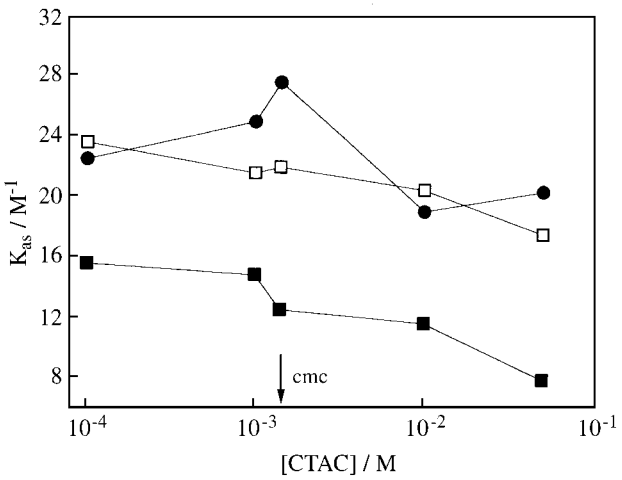

Figure 3. Apparent association constants as a function of CTAC concentration. (■) tryptophan , (•) IAA , (□) IBA.

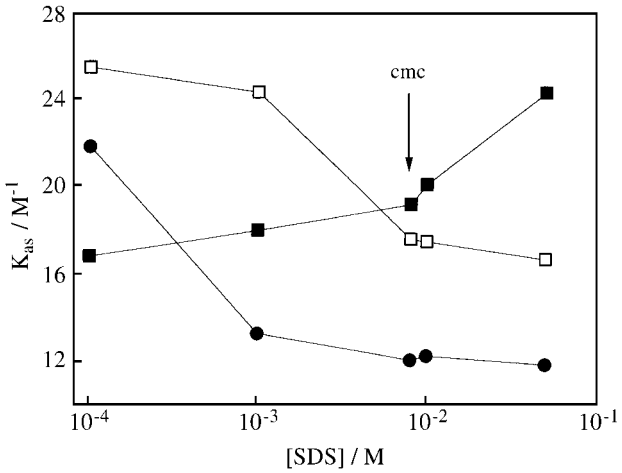

Figure 4. Apparent association constants as a function of SDS concentration. (■) tryptophan , (•) IAA , (□) IBA.

Reverse micelles

The typical charge-transfer band of indole derivatives with MV^{+2} is also present in reverse micelles of AOT in n-heptane. A representative spectrum is shown in Fig. 5 for IBA at different water/surfactant ratio (*R*). The similar characteristics of the spectrum in water and in reverse micellar solution (λ_{max} and spectral width) indicate that the association is taking place either in the water pool, or in the interface in a region with a very high water content. In these systems it is not possible to use high enough concentrations of MV^{+2} to have a complete saturation curve for the absorbance of the complex. Therefore, in order to evaluate the apparent association constant we used the initial slopes of the absorbance *vs.* $[MV^{+2}]$ and the extinction coefficient for the complex in water. The association constants as a function of the water content are presented in Fig. 6. The evaluation of K_{as} was based on the analytical concentration of the reactants. This is due to the lack of an easy and reliable means to determine local concentrations in the reverse micellar system. For the case of IAA the values of K_{as} are more than one order of magnitude greater in the reverse micelles than in water. The association constant is also very much higher than in water for IBA, while being of the same order for Trp. These results can be interpreted in terms a simple three pseudophase model[9]. At R = 5, the size of the water pool is negligible and the surfactant heads are incompletely hydrated. It was previously shown that indole alkanoic acids in AOT solutions are partitioned between the water pool and the interface[9]. IAA is mostly in the interface at low water content, and it is displaced to the water pool when R increases. Therefore, since MV^{+2} is expected to be localized at the negative interface, when R increases IAA moves from the interface to the center of the

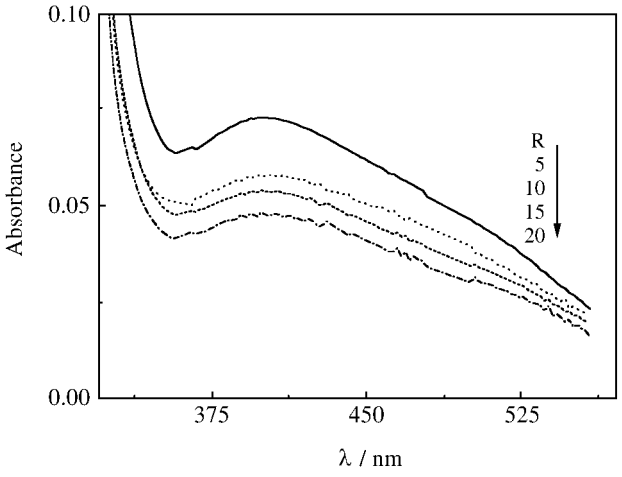

Figure 5. Absorption spectra of indolbutyric acid 9 x 10^{-4} M, MV^{+2} 1 x 10^{-3}; in AOT 0.2 M at different water contents (pH = 8).

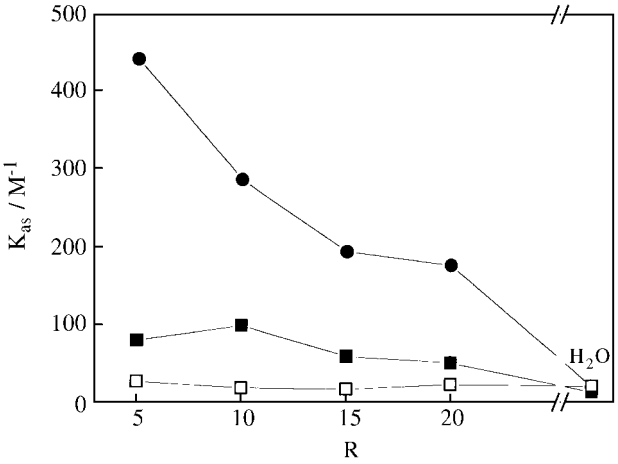

Figure 6. Apparent association constants in AOT reverse micelles as a function of the water content based on bulk indole concentration. (■) tryptophan , (•) IAA , (□) IBA.

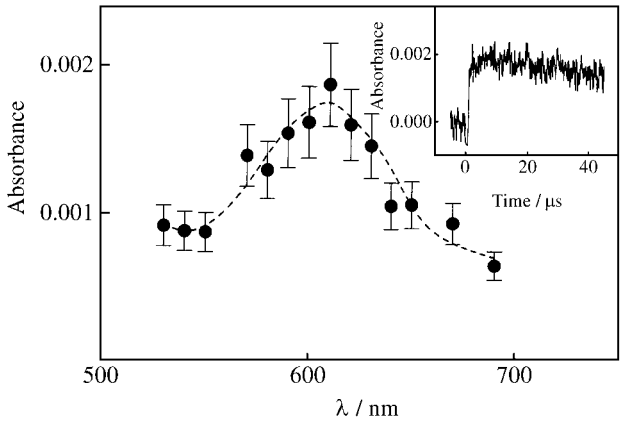

Figure 7. Transient absorption spectrum taken at 2 μs after laser pulse irradiation at 337 nm, of the Trp (0.01 M) - MV^{+2} (0.05 M) complex, in the presence of CTAC 0.1 M. Inset time profile of the absorption at 610 nm after irradiation at 355 nm.

water pool, the local concentration in the vicinity of MV^{+2} decreases and so does the apparent equilibrium constant. For Trp it was suggested that it remains in the interface independently of R. Therefore K_{as} shows only a minor change with the water content. In the case of IBA the values of the apparent association constants are of the same order of magnitude as in water. IBA is believed to co-micellize, forming part of the interface with most of the indole groups oriented towards the organic phase[12]. The emission spectrum of IBA in AOT at R = 5, corresponds to the indole group in an environment less polar than ethanol[12]. Nevertheless, the complex is weakly formed, due to the high concentration of MV^{+2} at the interface.

Laser photolysis results

When a solution containing Trp 0.01 M, MV^{+2} 0.05 M in CTAC 0.1M is laser flash irradiated at 337 nm or 355 nm a very weak, long lived (several tens of microseconds) absorption remains in the region of 600 nm. The absorption spectrum in the region around 600 nm resembles closely that of $MV^{+\cdot}$ [20] (Fig. 7). It must be noticed that for the concentrations referred to in Fig. 7, at 337 or 355 nm there is no appreciable absorption of the separate components of the solution. The quantum yield for $MV^{+\cdot}$ formation was estimated to be less than 0.001. This is very similar to the quantum yields for the similar processes observed by Hubig[4] in the case of naphthalene-MV^{+2} complexes. The radical cation was observed only in CTAC. In pure water or in SDS micelles we were not able to detect it. In reverse micelles, the absorption of the complex was too week to extract any valid conclusion. Also the absorption was very feeble in the case of IAA and IBA. These results may be explained by the electrostatic effect of the positive micelle/water interface. The methylviologen radical, carrying a positive charge, is probably partially expelled from the interface, and once in the water pseudo phase it becomes long lived. On the other hand for the negative SDS micelles, or even in CTAC for the negatively charged IAA and IBA the escape can not compete with a very fast recombination that may take place under these conditions.

Conclusions

The association constants for the EDA complexes formed by methylviologen and indole derivatives in normal cationic (CTAC) and anionic (SDS) micelles, depend on the surfactant concentration. This points to a micellar effect on the complex formation. It may be explained by considering the partitioning of the components between the aqueous and micellar pseudo phase

In the case of reversed micelles of AOT/ heptane, the apparent association constants for IAA and Trp are very much higher than in pure water or normal micellar solutions. They decrease with the water content of the solution. The observed behavior may be explained by the high local concentration of the reactants at the interface, and the subsequent displacement from the interface as the size of the water pool increases.

For IBA the values are of the same order of magnitude as in water due to the fact that IBA is forming part of the interface by a co-micellization process.

In normal micellar solution, laser flash photolysis of the complex produces the radical cation of methylviologen in low yield. This is only observed when the charge of the interface renders favorable the process of charge separation, which is the case of the cationic micelles of CTAC.

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