Use of the Brönsted equation in the interpretation of micellar effects in kinetics. Study of the reaction $[Fe(CN)_5(4\text{-}CNpy)]^{3-} + CN^- \rightleftarrows Fe(CN)_6{}^{4-} + 4\text{-}CNpy$ in SDS micellar solutions

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A study of the reaction $[Fe(CN)_5(4\text{-}CNpy)]^{3-} + CN^- \rightleftarrows Fe(CN)_6{}^{4-} + 4\text{-}CNpy$ was carried out in sodium dodecyl sulfate (SDS) micellar solutions. We conclude that the well known pseudophase model, an extension of the Olson–Simonson treatment to micellar solutions, is equivalent to the Brönsted equation in regard to rationalization of the micellar effects on reactivity. The equivalence follows from the fact that both pseudophase and Brönsted approaches can be used to rationalize kinetic data, as well as from thermodynamic considerations.

Micelles act as microreactors, compartmentalizing and concentrating or separating and diluting reactants and thereby altering, sometimes dramatically, apparent rate and equilibrium constants of chemical reactions.[1–3] Thus, micellar effects on the kinetics of chemical processes belong to the field of medium effects on chemical reactivity, a topic which has been of interest to chemists for over a century.[4] Additionally, micellar effects are connected to so-called *gated processes*.[5] These kinds of processes, which have recently received a great amount of attention in relation to biological reactions, have to do with the fact that in some cases, the reactants in their initial state present different configurations and the rate of interconversion of these configurations is comparable to the rate of the chemical reaction they experience. In the case of reactions in micellar systems, the "gated" character of the reactions would arise, not from a configurational change of the reactants, but from the coupling of the chemical process to the formation and dissociation of micellar aggregates,[6] as well as from the coupling of a chemical process to those of entering and/or leaving of one or both reactants in the micellar core.[7] From the above, interest in the studies of chemical reactivity in micellar systems is clear and, in particular, the fomulation of the results within the general context of medium effects on reactivity. This is the main purpose of our paper.

The pseudophase model[8] (PM) has been used to rationalize kinetic data in micellar solutions.[9,10] According to this model one (or both) reactants can be partitioned between the micellar and aqueous pseudophases in such a way that an equilibrium (partition) constant is defined as:

$$K = \frac{[S_m]}{[S_w][T]} \tag{1}$$

corresponding to the equilibrium:

$$S_w + T \rightleftarrows S_m \tag{2}$$

Here T is the micellized surfactant and S is the reactant being partitioned between the aqueous (w) and micellar (m) pseudophases.

When only one reactant is present in both pseudophases and the other remains in the aqueous pseudophase or is absent, it can easily be shown that the observed rate constant is given by:

$$k_{obs} = \frac{k_w + k_m K[T]}{1 + K[T]} \tag{3}$$

k_w and k_m being the pseudo-first- (or first-) order rate constants for the reactions in the aqueous and micellar pseudophases, respectively.

The application of the PM is nothing other than an adaptation of the Olson–Simonson model[11] to micellar systems. It can be demostrated that this model, frequently used in the interpretation of kinetic salt effects, is an alternative formulation to the Brönsted equation[12] (BE), which, as is well known, can be deduced from, that is, is consistent with transition state theory (TST). This equation for the reaction $A + B \rightarrow$ products is:

$$k_{obs} = k_0 \frac{\gamma_A \gamma_B}{\gamma_{\neq}} \tag{4}$$

In eqn. (4) γ_A, γ_B and $\gamma_{\neq}$ are the activity coefficients of the reactants and the activated state ($\neq$), respectively, and k_0 the rate constant for the reaction when it is carried out in the reference state.[13]

In this paper, taking as a basis the ligand substitution process (4-CNpy = 4-cyanopyridine):

$$[Fe(CN)_5(4\text{-}CNpy)]^{3-} + CN^- \rightleftarrows Fe(CN)_6{}^{4-} + 4\text{-}CNpy \tag{5}$$

we show the equivalence of the PM and BE formalisms. The relationships between the relevant parameters in both formulations are deduced.

The selected reaction presents (see below), some interesting advantages. First of all, the mechanism for this kind of process is well established.[14] They are dissociative in character, and proceed according to:

$$[Fe(CN)_5L]^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Fe(CN)_5{}^{3-} + L \tag{6a}$$

$$Fe(CN)_5{}^{3-} + L' \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [Fe(CN)_5L']^{4-} \tag{6b}$$

(in the present case L = 4-CNpy and L′ = CN⁻).

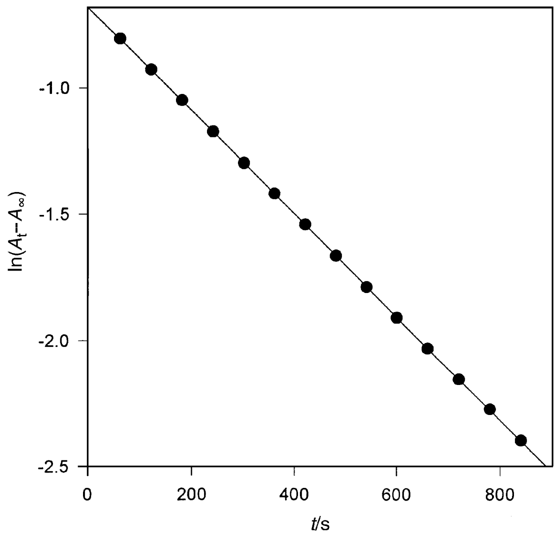

Fig. 1 Plot of $\ln(A_t - A_\infty)$ *vs.* t in a [SDS] = 0.3 mol dm^{-3} micellar solution: $[Fe(CN)_5(4\text{-}CN_{py})]^{3-} = 10^{-4}$ mol dm^{-3}, $[4\text{-}CN_{py}] = 10^{-3}$ mol dm^{-3}, $T = 298.2 \pm 0.1$ K.

On applying the steady state approximation for the concentration of $Fe(CN)_5{}^{3-}$, it can be shown that the rate equation is:

$$-\frac{d[Fe^{3-}]}{dt} = \frac{k_1k_2[Fe^{3-}][L'] - k_{-1}k_{-2}[Fe^{4-}][L]}{k_{-1}[L] + k_2[L']} \quad (7)$$

where $[Fe^{3-}] = [Fe(CN)_5L^{3-}]$ and $[Fe^{4-}] = [Fe(CN)_6{}^{4-}]$.

We checked in preliminary experiments that under the working conditions used in this study the contribution of the term containing k_{-2} in eqn. (7) can be neglected [that is, no dissociation of $Fe(CN)_6{}^{4-}$ was detected]. Consequently, this equation becomes:

$$-\frac{d[Fe^{3-}]}{dt} = \frac{k_1k_2[Fe^{3-}][L']}{k_{-1}[L] + k_2[L']} = k_{obs}[Fe^{3-}] \quad (8)$$

with

$$k_{obs} = \frac{k_1k_2[L']}{k_{-1}[L] + k_2[L']} \quad (9)$$

Eqn. (9) shows that by working at different concentrations of L and L′ it is possible to range between *true* second-order kinetics (when $k_{-1}[L] \gg k_2[L']$ and [L] = constant) to *true* first-order kinetics (when $k_{-1}[L] \ll k_2[L']$). The latter case corresponds to measuring the rate constant for the dissociation process in eqn. (6*a*). So, it is possible to study the micellar influence on first- and second-order processes separately by adequately choosing the experimental conditions.

Experimental

Materials

$Na_3[Fe(CN)_5(NH_3)]\cdot 3H_2O$ was prepared according to the method in reference 15 and characterized by UV–VIS absorption spectra and CHN microanalysis. The other reagents were all Anala R grade and used as purchased, except the 4-CNpy ligand, which was of lower purity. This reagent was purified as indicated in reference 16. Dodecyl sulfate sodium salt (Merck purity >99%) was stored in a vacuum desiccator over P_2O_5 for several days before use. The water used in preparation of the solutions had a conductivity of $\sim 10^{-6}$ S m^{-1}. The water was also deoxygenated before use.

Kinetics

Rate measurements were performed by following the absorbance changes of the solutions containing the reactants and the surfactant at the desired concentrations. The absorbance due to the $[Fe(CN)_5(4\text{-}CN_{py})]^{3-}$ complex was measured at $\lambda = 477$ nm. The $[Fe(CN)_5(4\text{-}CNpy)]^{3-}$ complex was prepared *in situ* from $[Fe(CN)_5(NH_3)]^{3-}$ and the 4-CNpy ligand. The ammonia complex, as is known,[17] undergoes rapid hydrolysis, to produce the corresponding aquo complex $[Fe(CN)_5(H_2O)]^{3-}$. This complex in the presence of an excess of 4-CNpy $\{[Fe(CN)_5(NH_3)^{3-}] = 10^{-4}$ mol dm^{-3} and $[4\text{-}CNpy] = 10^{-3}$ mol $dm^{-3}\}$ produces instantaneously $[Fe(CN)_5(4\text{-}CNpy)]^{3-}$. Once the reactant was formed as indicated, the other reagents and the surfactant were added. The pH of the solutions was kept constant at a value of 11.7 in order to avoid hydrolysis of the CN^- ion. The concentration of this ion was always greater than those of the iron complex (see tables). When the concentration of CN^- ion was lower than 0.2 mol dm^{-3} the ionic concentration in the solutions was kept constant by adding NaCl.

The rate constants, k_{obs}, were obtained from the slopes of $\ln(A_t - A_\infty)$ *vs.* t plots, A_t and A_∞ being the absorbance measured at time t and the final absorbance, respectively. No less than three determinations were made to contribute to each rate constant value and were found to be reproducible within 3%. A representative plot appears in Fig. 1.

Results

Table 1 gives k_{obs}, the pseudo-first-order rate constant in SDS micellar solutions at different concentrations of CN^- ion. As indicated in the introduction, these rate constants are given by eqn. (9). According to this equation, when the concentration of 4-CNpy ligand is maintained constant, an asymptotic behavior is expected for k_{obs} as the concentration of CN^- is increased. For high CN^- values, the limiting value is k_1 [see eqn. (6)]. Fig. 2 shows this behavior in an SDS solution. As can be seen in the figure, the limiting value of $k_{obs} = k_1$ is obtained for $[CN^-] \geq 0.1$ mol dm^{-3}. Accordingly, the values of k_{obs} in Table 1 corresponding to $[CN^-] = 0.2$ mol dm^{-3} are in fact k_1 values. Note that these k_1 values are practically independent of the SDS concentration.

Eqn. (9) can also be written as:

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}[4\text{-CNpy}]}{k_1k_2}\frac{1}{[CN^-]} \quad (10)$$

and a plot of k_{obs}^{-1} *vs.* $[CN^-]^{-1}$ has a slope of $k_{-1}[4\text{-CNpy}]/k_1k_2$. From this slope, taking into account that k_1 and

Table 1 Pseudo-first-order rate constant ($10^4k_{obs}/s^{-1}$) in SDS (mol dm^{-3}) micellar solutions at different concentrations of CN^- ion at 298.2 ± 0.1 K: $[Fe(CN)_5(4\text{-}CN_{py})]^{3-} = 10^{-4}$ mol dm^{-3}, $[4\text{-}CN_{py}] = 10^{-3}$ mol dm^{-3}

	$[CN^-]$/mol dm^{-3}					
[SDS]	0.2	0.08	0.05	0.02	0.01	0.003
0.008	9.10	7.10	6.59	4.24	2.38	0.94
0.10	9.35	7.89	7.26	5.43	3.44	1.29
0.16	9.20	8.70	7.71	5.53	3.89	1.48
0.23	8.98	8.80	7.64	6.43	4.58	1.83
0.30	8.87	9.16	7.84	7.02	4.62	2.13

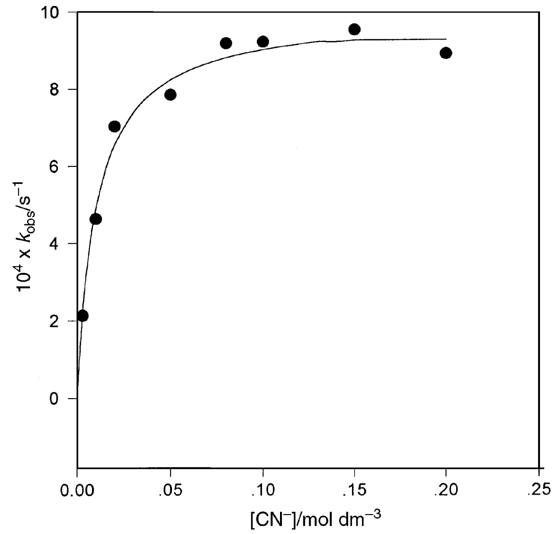

Fig. 2 Plot of the pseudo-first-order rate constant (k_{obs}) at different CN^- concentrations in [SDS] = 0.3 mol dm^{-3} micellar solutions.

[4-CNpy] are known, the ratio k_2/k_{-1} can be obtained. The values of this relation for SDS solutions appear as k_2^{rel} in Table 2. Notice that according to eqn. (6), k_2^{rel} represents the rate constant for the reaction of CN^- with $Fe(CN)_5{}^{3-}$, relative to the rate constant for the reaction of 4-CNpy with the same iron moiety.

Discussion

As mentioned above, k_1 in SDS solutions is not dependent on the surfactant concentration. Taking into account that this rate constant corresponds to the dissociation of a ligand in a *negatively* charged complex, this is the behavior to be expected: this implies that, on average, this dissociation happens far from the micellar surface and, indeed, long range influences of the charged micelles do not operate significantly on this process.

As to the k_2^{rel} rate constant in Table 2, it increases as the SDS concentration increases. Fig. 3 shows plots of k_2^{rel} and $\log(k_2^{rel})$ *vs.* [SDS]. It is difficult to decide from these plots what is the variation law of k_2^{rel}. The linear behavior can be rationalized by using the pseudophase model, under the (reasonable) assumption that K[T] in eqn. (3) is $\ll 1$. We thus obtained $(k_2^{rel})_w$ and $K(k_2^{rel})_m$ by fitting the values of k_2^{rel} in Table 2 to the equation:

$$k_2^{rel} = (k_2^{rel})_w + (k_2^{rel})_m K[T] \qquad (11)$$

The values of k_2^{rel} calculated from eqn. (11) and the fitted values of $(k_2^{rel})_w$ and $K(k_2^{rel})_m$ are given in Table 2.

Table 2 Relative rate constant, k_2^{rel}, obtained from the experimental data and the adjusted values obtained for this parameter using the pseudophase model (PM) and Brönsted equation (BE), respectively, in several SDS (mol dm^{-3}) micellar solutions. Experimental conditions as in Table 1

[SDS]	k_2^{rel}	PM[a]	BE[b]
0.008	0.034	0.036	0.039
0.10	0.049	0.055	0.053
0.16	0.058	0.068	0.064
0.23	0.075	0.082	0.081
0.30	0.090	0.097	0.101

[a] Calculated from eqn. (11) and the following parameter values: $(k_2^{rel})_w = 0.0342$ and $K(k_2^{rel})_m = 0.211$ mol^{-1} dm^3. [b] Calculated from $\log k_2^{rel} = \log(k_0)_2^{rel} + C[T]$ with $(k_0)_2^{rel} = 0.038$ [or $\log(k_0)_2^{rel} = -1.420$] and $C = 1.431$.

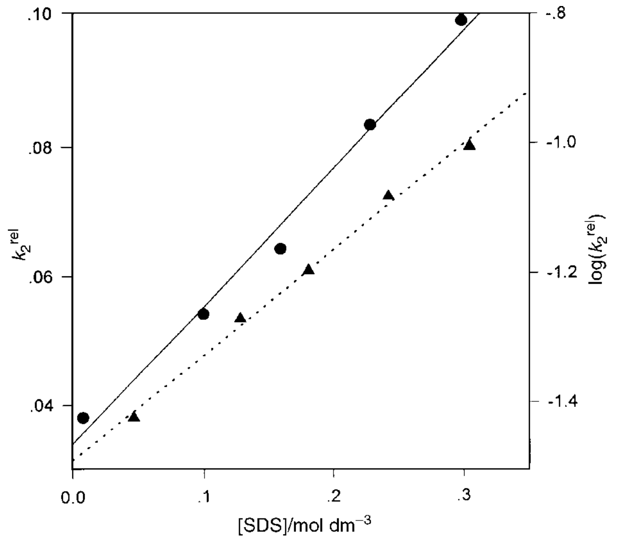

Fig. 3 Plots of k_2^{rel} and $\log(k_2^{rel})$ at different micellized SDS concentrations. (●) k_2^{rel} experimental data; (——) calculated from PM; (▲) $\log(k_2^{rel})$ experimental data; (···) calculated from BE.

The logarithmic plot can be interpreted according to the ideas presented in the introduction, taking as the starting point BE [eqn. (4)]. Of course, the use of this equation requires calculation of the activity coefficients. This calculation can be done in dilute salt solutions by using the Debye–Hückel formalism. However, this formalism implies consideration of the ions in the ionic cloud of the central ion as point charges. Although this is a reasonable approximation in dilute (conventional) electrolyte solutions, it does not seem to be adequate for micellar solutions because of the size of the micelles. Thus, it is better to use an extended Debye–Hückel formalism in order to take into account the excluded volume effects. According to this:

$$\log \gamma_i = \frac{-A'' z_i^2 \sqrt{[T]}}{1 + B''\sqrt{[T]}} + \phi([T]) \qquad (12)$$

This equation takes into account that the ionic strength produced by the micelles is proportional to its concentration and that the excluded volume effect represented by the $\phi([T])$ term depends on the concentration of the micelles.[18] This term, in concentrated electrolyte solutions, can be approximated by a linear term,[19] thus eqn. (12) becomes:

$$\log \gamma_i = \frac{-A'\sqrt{[T]}}{1 + B'\sqrt{[T]}} + C'[T] \qquad (13)$$

Consequently, taking the logarithm in eqn. (4) and substituting eqn. (13) results in:

$$\log k_2^{rel} = \log(k_0)_2^{rel} + \frac{A\sqrt{[T]}}{1 + B\sqrt{[T]}} + C[T] \qquad (14)$$

According to this equation, the linear behavior of $\log k_2^{rel}$ *vs.* [T] can be explained by assuming that the term containing $[T]^{1/2}$ is a constant at the high ionic strength produced by the micelles.[20]

Therefore, it is concluded that both the pseudophase model and BE are equivalent (in the sense that both can be used to rationalize kinetic data in micellar systems). In fact, the linear dependence of k_2^{rel} on [T] is a particular case of the logarithmic dependence, as can easily be shown by taking in the expresion of the logarithmic equation written as $k = k_0\, e^{C[T]}$ only the linear term in the expansion of the exponential term. In this regard, BE comprises a particular case of PM.

In order to go further we will establish the relationships between the relevant parameters in both models. These relationships will be deduced for a first-order process to simplify calculations, but the results can be extended to processes with any reaction order.

Consider the reaction $S \rightarrow (\neq) \rightarrow P$ coupled to a partition between two phases (or pseudophases), w and m, described by eqn. (2) and with an equilibrium constant defined as in eqn. (1). The observed rate constant, k_{obs}, can be obtained in terms of the rate constant in phase w as follows. From a kinetic point of view, for a unimolecular processes, k_{obs} and k_i (i = w, m) are defined from the following equations:

$$k_{obs} = -\frac{1}{[S]}\frac{d[S]}{dt} \tag{15a}$$

$$k_i = -\frac{1}{[S]_i}\frac{d[S]_i}{dt} \tag{15b}$$

where the concentrations refer to the total volume of the system V. Accordingly:

$$[S]_w = \frac{[S]}{1 + K[T]} \tag{16a}$$

$$[S]_m = \frac{[S]K[T]}{1 + K[T]} \tag{16b}$$

$$[S]_w + [S]_m = [S] \tag{16c}$$

If $[S]^i$ represents the concentration of S in phase i, referred to the volume of phase i, V_i, it is clear that:

$$[S]^i = \frac{[S]_i V}{V_i} \tag{17}$$

So, the *local* rate constant k^i, defined as:

$$k^i = -\frac{1}{[S]^i}\frac{d[S]^i}{dt} \tag{18}$$

is the same as k_i defined in eqn. (15*b*) because *for a unimolecular process* the volume terms cancel. That is, according to TST:

$$(\Delta G^{\neq})_i = (\Delta G^{\neq})^i \tag{19}$$

The latter activation free energy is given by:

$$(\Delta G^{\neq})^i = [\mu^{0'}(\neq)]^i - [\mu^{0'}(S)]^i \tag{20}$$

$[\mu^{0'}(\alpha)]^i$ being the standard formal chemical potential of species α ($\alpha = \neq$, S) in the phases i (i = w, m).

On the other hand, the existence of an equilibrium for S between phases m and w implies:

$$\mu_w(S) = \mu_m(S)$$
$$\mu_w(\neq) = \mu_m(\neq) \tag{21}$$

(The second equation follows from TST and the zeroth law of thermodynamics).
According to this, one can write:

$$[\mu^{0'}(\alpha)]^w + RT\ \ln[\alpha]^w = [\mu^{0'}(\alpha)]^m + RT\ \ln[\alpha]^m \tag{22}$$

or, using eqn. (17):

$$[\mu^{0'}(\alpha)]^m = [\mu^{0'}(\alpha)]^w + RT\ \ln\frac{[\alpha]_w V_m}{[\alpha]_m V_w} \tag{23}$$

Taking into account that:

$$\frac{[\alpha]_w}{[\alpha]_m} = \frac{1}{K_\alpha[T]} \tag{24}$$

eqn. (23) becomes:

$$[\mu^{0'}(\alpha)]^m = [\mu^{0'}(\alpha)]^w + RT\ \ln\frac{V_m}{V_w K_\alpha[T]} \tag{25}$$

From this equation and eqns. (19) and (20) it follows that:

$$(\Delta G^{\neq})_m = (\Delta G^{\neq})_w + RT\ \ln\frac{K}{K_{\neq}} \tag{26}$$

Substituting k_{obs} and k_i in eqn. (3) by

$$k_{obs} = Ae^{-(\Delta G^{\neq})_{obs}/RT}$$
$$k_i = Ae^{-(\Delta G^{\neq})_i/RT} \tag{27}$$

and using eqn. (26) it follows that:

$$e^{-(\Delta G^{\neq})_{obs}/RT} = e^{-(\Delta G^{\neq})_w/RT}\left(\frac{1 + K_{\neq}[T]}{1 + K[T]}\right) \tag{28}$$

Consequently:

$$k_{obs} = k_w\left(\frac{1 + K_{\neq}[T]}{1 + K[T]}\right) \tag{29}$$

In order to show the equivalence of eqns. (29) and (3) we must prove that $k_w K_{\neq} = k_m K$. This equation is easily proved in the following way. By definition:

$$k_w = Ae^{-[\mu^{0'}(\neq)^w - \mu^{0'}(S)^w]/RT}$$
$$K_{\neq} = Be^{-[\mu^{0'}(\neq)^m - \mu^{0'}(\neq)^w]/RT} \tag{30}$$

So

$$k_w K_{\neq} = ABe^{-[\mu^{0'}(\neq)^m - \mu^{0'}(S)^w]/RT} \tag{31}$$

On the other hand:

$$k_m = Ae^{-[\mu^{0'}(\neq)^m - \mu^{0'}(S)^m]/RT}$$
$$K = Be^{-[\mu^{0'}(S)^m - \mu^{0'}(S)^w]/RT} \tag{32}$$

Thus:

$$k_m K = ABe^{-[\mu^{0'}(\neq)^m - \mu^{0'}(S)^w]/RT} \tag{33}$$

Comparing eqns (31) and (33) it is seen that $k_w K_{\neq}$ is identical to $k_m K$.

On the other hand, for a first-order process,

$$k_{obs} = k_w\frac{\gamma_s}{\gamma_{\neq}} \tag{34}$$

(taking as the reference state that corresponding to the reaction in water). Obviously, eqn. (34) is also consistent with the general eqn. (29) if we take for a given species, i,

$$\gamma_i = \frac{1}{1 + K_i[T]} \tag{35}$$

K_i being the equilibrium constant corresponding to the distribution of species i between the aqueous and micellar pseudophases.

In conclusion, the results obtained in this paper confirm the idea that the Pseudophase Model and the Brönsted Equation are equally valid approaches for the interpretation of kinetic data in micellar systems and for any reaction order process. In fact, this conclusion simply extends the similar one reached by Scatchard[21] for kinetic salt effects: the equivalence of the approaches based on the Brönsted Equation and Olson–Simonson model.

Acknowledgements

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