

# Thermodynamics and Kinetics in Micellar Media. Reaction of the Hydroxide Ion with 1,3,5-Trinitrobenzene in Aqueous Solutions of a Neutral Nonionic Surfactant. Effect of the Concentration of Background Electrolyte

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The use of a neutral surfactant (Brij 35) allows us to investigate its influence upon the kinetics of the reaction between a neutral substrate and a charged reactant. The thermodynamic description of a micellar system can be obtained by introducing a variable of area in the expression of the internal energy. Thus, the content of micellar solutions is separated into two components: a volume content associated with dimension 3, and an area content associated with dimension 2. The volume is an extensive parameter and a homogeneous function of degree unity of its content, but the area is not necessarily an extensive function and does not vary linearly with content. In this way, we can describe the evolution of the behavior of micellar solutions when the concentration of surfactant increases. We introduce the notion of “micellar catalysis” in terms of an increase of the exchange rate at equilibrium,  ${}^m\nu_0$ , for the studied reaction. The formal separation of the content of the solution into two components with different dimensions leads us to suppose a difference in reactivity. The exchange rate associated with the content of dimension 2 equals 40 times the one associated with the content of dimension 3.

## I. Introduction

The kinetics of the bimolecular reaction between a neutral substrate and a charged reagent is usually strongly modified, in aqueous solutions, by the presence of micellar aggregates of ionic surfactants whose charge is opposite in sign to that of the ionic reagent. This phenomenon of “micellar catalysis” has been investigated by many teams of researchers for several systems.<sup>1–8</sup> In general, it has been attributed to the effects of local high concentrations of the neutral reagent within the micellar aggregates and of the charged reagent close to the polar headgroups of the amphiphile ions. Many models have been proposed to explain this behavior.

In particular, the micellar media have often been described by means of electrically charged pseudophase models.<sup>9–16</sup> In previous work<sup>17</sup> concerning the nucleophilic addition of the hydroxide ion to 1,3,5-trinitrobenzene (TNB) in water, and in various aqueous solutions with several concentrations of background electrolyte, using the cationic surfactants dodecyltrimethylammonium bromide (DTABr) and hexadecyltrimethylammonium bromide (CTABr), we have shown that this kind of approach could not explain the whole of the kinetic and thermodynamic effects observed, in particular when one increased the amount of surfactant in solution. One of the main and outstanding results of our study has been to show that it was indispensable to introduce at least a variable of area into the thermodynamic and kinetic description of the phenomena, and that in a great number of cases this area increased faster than the mass of the added surfactant.

To benefit from the strong electric contribution to the catalysis phenomenon, most of the investigations have been carried out with charged surfactant solutions.<sup>8,18</sup> On the other hand, few studies have investigated bimolecular reactions between a neutral

reagent and an ionic species in the presence of micelles of neutral amphiphiles.<sup>7c,19</sup> However, this system must be investigated with care. Indeed, if one carefully analyzes the values of the equilibrium and rate constants obtained in the case of catalysis by the cationic amphiphiles (DTABr and CTABr), for example for the addition of hydroxide ion to 1,3,5-trinitrobenzene, one notices an important acceleration of the rate of attack by  $\text{OH}^-$  relative to that in water and simultaneously a strong decrease in the reverse rate of reaction corresponding to the destruction of the monoadduct. Thus, there is a large increase in the value of the equilibrium constant. This behavior can be ascribed to strong stabilization of the activated complex by the charged micellar medium.

This fact seemed interesting to us, and we have tried to examine the influence of the charge of the amphiphile on the stabilization of the activated complex by studying the kinetic and thermodynamic components of the test addition reaction of hydroxide ion to TNB in aqueous solutions of a neutral surfactant, dodecylpoly(oxyethyleneglycol ether)<sub>n</sub>, ( $n = 23$ , Brij 35).

According to the literature, the terminal hydroxyethyl group of a molecule of Brij 35 should be partially deprotonated at high pH, giving the corresponding alkoxide ions which should be able to react, in competition with  $\text{OH}^-$ , in the nucleophilic aromatic substitution.<sup>6c</sup> In this work, we have checked kinetically that the rate constant of the addition to the TNB, in micellar solutions of dodecyltrimethylammonium bromide (DTABr), did not depend on Brij 35, whatever its concentration was. Furthermore, the  $\sigma$  complex formed has the same visible spectrum as the one corresponding to TNBOH in aqueous solutions of neutral zwitterionic or ionic surfactants. Consequently, we have considered, in this paper, that the adduct  $\text{TNBOH}^-$  was the only one formed. To maintain constant ionic strength, we used two different concentrations of background electrolyte, 0.1 and 0.3  $\text{mol}\cdot\text{dm}^{-3}$  NaBr.

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## II. Materials, Methods and Measurements

**1. Materials.** 1,3,5-Trinitrobenzene (TNB) and dodecylpoly-(oxyethyleneglycol ether)<sub>n</sub> (*n* = 23, Brij 35) came respectively from the Tokyo Kasei and the Aldrich companies. These products were used with no further purification. A stock solution of Brij 35 was prepared at the beginning of the study and was used for all the measurements. It was protected from heat and light.

Sodium hydroxide (NaOH) and sodium bromide (NaBr) were from Acros Organics.

All the solutions were prepared with distilled water.

The critical micellar concentrations (cmc's) of Brij 35 were determined for both salt media by surface tension measurements<sup>20</sup> with a Krüss K10ST apparatus. Their values are respectively  $7.9 \times 10^{-5}$  and  $2.9 \times 10^{-5}$  mol dm<sup>-3</sup> in 0.1 and 0.3 mol dm<sup>-3</sup> NaBr at 298 K.

We used our previous approach for the interpretation of the results.<sup>17</sup> Some experimental values, and the main reasoning and relations, will be recalled during the discussion of the experimental values.

**2. Kinetic measurements** were made on an Applied Photo-physics SX18 MV stopped-flow spectrophotometer. The temperature was maintained at 298 K by circulating water from a thermostated bath around the injection syringes and the reaction cell. To reduce the mixing time, we carried out the experiments by filling the injection syringes with solutions containing the same concentration of surfactant and NaBr. Pseudo-first-order conditions of the reaction were assured by using a large excess of sodium hydroxide over TNB. As for the previous study,<sup>17</sup> we were interested only in the formation of the monoadduct TNBOH<sup>-</sup>.

**3. Solubility measurements** of TNB in Brij 35 solutions were carried out by introducing an excess of recrystallized solid TNB into 10 mL of surfactant solution and stirring for 36 h in a thermostated bath at 298 K. The solutions were then centrifuged and left at rest at the same temperature for half an hour. The analysis of the supernatant was carried out by UV-visible spectrophotometry at 320 nm.

## III. Experimental Section

The reaction for the addition of OH<sup>-</sup> ion to TNB can be schematized by



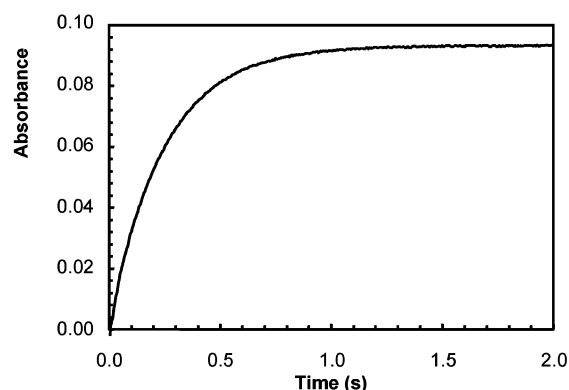
<sup>m</sup>k<sub>1</sub> and <sup>m</sup>k<sub>-1</sub> are respectively the forward and reverse rate constants of the reaction studied. The values of the equilibrium constant <sup>m</sup>K are calculated from the ratio of these forward and reverse rate constants:

$${}^mK = \frac{\{^m k_1\}}{\{^m k_{-1}\}} \quad (2)$$

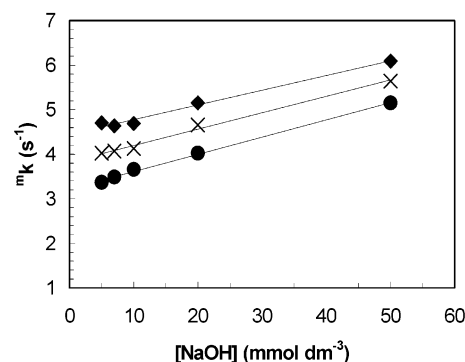
For all the measurements realized, the kinetics observed corresponding to the addition of OH<sup>-</sup> to TNB are first order as a function of the base concentration. This is illustrated in Figure 1. For all the solutions studied above the cmc, the apparent rate constant <sup>m</sup>k fits relation (3) even for the smallest OH<sup>-</sup> concentrations:

$${}^m k = {}^m k_1 [OH^-] + {}^m k_{-1} \quad (3)$$

Figure 2 presents some of these results. Table 1a lists the



**Figure 1.** Variation of absorbance as a function of time in 0.012 mol dm<sup>-3</sup> Brij 35, 0.3 mol dm<sup>-3</sup> NaBr, 10<sup>-2</sup> mol dm<sup>-3</sup> NaOH, and 4 × 10<sup>-5</sup> mol dm<sup>-3</sup> TNB.



**Figure 2.** Variation of <sup>m</sup>k as a function of NaOH concentration in 0.3 mol dm<sup>-3</sup> NaBr for various Brij 35 concentrations: ♦, 0.010 mol dm<sup>-3</sup>, ×, 0.012 mol dm<sup>-3</sup>, ●, 0.016 mol dm<sup>-3</sup>.

values of <sup>m</sup>k<sub>1</sub>, <sup>m</sup>k<sub>-1</sub>, and <sup>m</sup>K obtained in Brij 35 micellar medium in 0.1 and 0.3 mol dm<sup>-3</sup> NaBr for various amounts of aggregated surfactant, denoted *x*:

$$x = {}^mC - \text{cmc} \quad (4)$$

where <sup>m</sup>C is the total concentration of surfactant in solution.

A marked shift of the equilibrium to increased formation of the monoadduct is observed in the presence of neutral surfactant. This effect, which increases with the amount of surfactant, results from a small increase in the value of the forward rate constant and a concomitant large decrease in the value of the reverse rate constant. These effects can be compared to those obtained for the same reaction with cationic surfactants in similar conditions of micellization (same concentration of micellized surfactant *x*, Table 1b).

We have established that the values of the forward rate constants are larger (from 3 to 11 times higher) in the case of cationic surfactants. This confirms the importance of the electric contribution to the catalytic phenomenon. We can also question whether the small increase in the values of the forward rate constants in the Brij 35 media is not of identical origin. Indeed, Akbas et al.<sup>22</sup> assume that sodium ions are susceptible to being partially retained by the micelles, which could make them positively charged. Thus, we could suppose that there is a small electrostatic contribution to the increase in the forward rate. The decrease of this effect by screening when background electrolyte is added would also work in this direction.

We observe a large decrease of the value of the reverse rate constant in the presence of neutral surfactant which is, however, less than that which occurs in the presence of cationic am-

**TABLE 1: Values of  ${}^m k_1$ ,  ${}^m k_{-1}$ , and  ${}^m K$  in (a) Brij 35 and (b) DTABr<sup>a</sup>**

(a) In Brij 35				
$x$ (mmol dm <sup>-3</sup> )	${}^m k_1$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	${}^m k_{-1}$ (s <sup>-1</sup> )	${}^m K$	
In Water <sup>21</sup>				
—	37.5	9.8	3.8	
In 0.1 mol dm <sup>-3</sup> NaBr at 298 K (cmc = 0.079 mmol dm <sup>-3</sup> )				
7.9	42	4.08	10	
9.9	42	3.67	11	
15.9	44	2.98	15	
19.9	48	2.55	19	
23.9	47	2.31	20	
29.9	48	2.07	23	
49.9	51	1.59	32	
In 0.3 mol dm <sup>-3</sup> NaBr at 298 K (cmc = 0.029 mmol dm <sup>-3</sup> )				
8.0	34	5.07	7	
10.0	35	4.41	8	
12.0	37	3.82	10	
16.0	42	3.18	13	
20.0	41	2.78	15	
24.0	41	2.52	16	
30.0	41	2.23	18	
50.0	44	1.70	26	
(b) In DTABr				
[DTABr] (10 <sup>-3</sup> mol dm <sup>-3</sup> )	$x$ (10 <sup>-3</sup> mol dm <sup>-3</sup> )	${}^m k_1$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	${}^m k_{-1}$ (s <sup>-1</sup> )	${}^m K$
In 0.1 mol dm <sup>-3</sup> NaBr				
7.0	2.5	114	1.39	82
8.0	3.5	138	1.22	113
10.0	5.5	178	1.09	163
12.8	8.3	228	0.99	230
17.6	13.1	310	0.90	344
20.0	15.5	340	0.99	343
In 0.3 mol dm <sup>-3</sup> NaBr				
8.0	5.7	72	1.58	46
16.0	13.7	120	1.18	102
24.0	21.7	160	1.04	154
32.0	29.7	188	0.98	192
40.0	37.7	212	0.96	221
48.0	45.7	231	0.93	248
56.0	53.7	246	0.93	265
64.0	61.7	261	0.92	284

<sup>a</sup> The errors in the values are estimated at  $\pm 5\%$ .

phiphiles. The addition of background electrolyte causes a small increase in these values.

We establish that, above the micellization threshold, the addition of neutral surfactant in solution involves a notable modification of the thermodynamic and kinetic parameters of the reaction. The effect is of lower magnitude than in the case of charged surfactants, but it is not negligible.

Using the approach previously described,<sup>17</sup> we can analyze the way the kinetic and thermodynamic parameters of the reaction are modified by the presence of the neutral surfactant.

#### IV. Interpretation

**1. Fundamental Aspects.** We developed a thermodynamic approach in a previous paper<sup>17</sup> which takes into account a variable of area,  ${}^a A$ , in the Gibbs energy function. We have more or less associated this parameter with micellar structure, but this physical picture is not thermodynamically necessary, and we can consider that the area is a variable of dimension 2 that is indispensable in the functions of state used to describe correctly the behavior of the system. This area is not a geometrically defined surface.

With this modification, we do not have to consider micelles as clearly defined objects. The labile behavior of micellar

aggregates implies that they develop and break down continually.<sup>23–27</sup> Every point of the solution can thus be considered as being in turn within the micelle, and then at the surface, and then in its surroundings. Obviously, a description of the micellar solution using the static phase-separation model does not fit in with the reality. The introduction into the thermodynamic and kinetic relations of a variable of state of dimension 2 reflects the multiplicity of dimensions that the micellar aggregates may have.

The introduction of some variable of dimension into the equations of state implies that they can be associated with some component of mass without their precise location in the system being known.

Indeed, we consider that the Gibbs energy  $G$  of a system made up of  $n_1$  moles of solvent,  $n_2$  moles of surfactant, and  $n_i$  moles of solute  $i$  is written

$$dG = V dP - S dT + \mu_1 dn_1 + \mu_2 dn_2 + \mu_i dn_i + \gamma dA$$

where  $\gamma$  is the interfacial tension associated with the area variable.

Then, the properties of the partial derivatives imply the following equality:

$$\left(\frac{\partial \gamma}{\partial \mu_2}\right)_{T,P,A,n_1,n_i} = -\left(\frac{\partial n_2}{\partial A}\right)_{T,P,\mu_2,n_1,n_i} \quad (5)$$

If we consider that  $\gamma$  is capable of varying with the chemical potential of component 2, then the right-hand term of this relation is nonzero. This means that when the area term is modified for a constant chemical potential of 2 ( $T, P, n_1$ , and  $n_i$  constant), then the amount of 2 in the system must also be modified. This double condition is possible only if a certain number of moles of 2 is associated with the area, denoted  ${}^a n_2$ . The remaining moles of 2 will be conventionally attributed to the variable of dimension 3, the volume. They will be denoted  ${}^b n_2$ . The number of molecules of 2 in solution is then divided between the two environments of different dimension, as

$$n_2 = {}^a n_2 + {}^b n_2 \quad (6)$$

There is no requirement that these environments should constitute geometrically separate and identifiable domains; they are, in fact, an abstraction.

By convention, we will suppose that the micellized surfactant belongs exclusively to the area environment and that the number of molecules of the solute  $i$  is divided in the same way:

$$n_i = {}^a n_i + {}^b n_i \quad (7)$$

In the case of the solvent, we assume that a small modification of its amount in the system does not involve any change of  $\gamma$  [ $(\partial \gamma / \partial \mu_2)_{T,P,A,n_1,n_i} = 0$ ]. Then, the area environment does not have any contribution due to solvent 1:  $n_1 = {}^b n_1$ .

Thus, the area term depends on the system content of 2 and  $i$ , and we can write, at constant  $T$  and  $P$ ,

$${}^a A = {}^a A({}^a n_2, {}^a n_i) \quad (8)$$

Unlike volumes, areas are not necessarily extensive functions. This means that when the number of moles occupying the area environment is multiplied by a number  $\lambda$ , the area itself would not necessarily be multiplied by  $\lambda$ .

When we accept that the area is not a homogeneous function of degree unity of the content of the system, then neither are

the internal energy and the other functions of state. They lose their extensivity property. Their derivatives with respect to the mass variables do not give variables independent of the content of the system. This problem directly concerns the behavior of micellar solutions when the amount of micellized surfactant increases in the medium.

In the pseudophase model, where solutes are supposed to be retained within the perfectly defined micelles, if the amount of aggregated surfactant is multiplied by a number  $\lambda$ , the "volume of the micellar phase" is then multiplied by the same number. If the micellar content is associated with an area and not a volume, the same does not necessarily apply, because the area may not vary linearly with the content. We have formalized this by attributing to the area the property of being a Euler function of degree  $p$  of the micelles associated with the area. If the micellar area component is multiplied by  $\lambda$ , then the area is multiplied by  $\lambda^p$ .

Euler's relations allows us to express the area as a function of the partial areas:

$$p^\sigma A = \sigma n_2^\sigma A'_2 + \sigma n_i^\sigma A'_i \quad (9)$$

Thus, we have an additional degree of freedom to explain the behavior of a dispersed medium when the amount of aggregates in solution is modified.

In the particular case where the area is a homogeneous function of degree unity of its content, the exploitation of the results is strictly identical to that in the pseudophase model. In the other cases, it is possible to verify that the area is a Euler function and to determine the value of  $p$ . Even though the contents of area and of volume are not distinguishable, the different relations between their compositions can be expressed, knowing that, in a system at equilibrium, the affinity<sup>28</sup> is equal to zero.

The following relationships have been developed in our previous work.<sup>17</sup>

We show that the molar fraction of the component  $i$  in dilute solution, in the area content, defined by

$$\sigma X_i = \frac{\sigma n_i}{\sigma n_i + \sigma n_2} \approx \frac{\sigma n_i}{\sigma n_2} \quad (10)$$

and the concentration of  $i$  in the volume content  ${}^b C_i = {}^b n_i/V$ , are linked by

$$\sigma X_i = \{{}^b C_i\} \varphi_i \quad (11)$$

The coefficient  $\varphi_i$  is of the general form

$$\varphi_i = \left\{ \frac{\sigma A'_2}{p} \right\} \exp\left( \frac{{}^b \mu_i^\theta - \sigma \mu_i^\theta}{RT} \right) \exp\left( \frac{z_i F({}^b \phi - \sigma \phi)}{RT} \right) \exp\left( - \frac{\sigma \gamma^\sigma A'_i}{RT} \right) \quad (12)$$

The exponential terms are grouped together under a retention coefficient,  $\varphi_i$ . This takes into account the classical contributions which concern the differences in environment of the solute when it belongs to the area or to the volume content ( ${}^b \mu_i^\theta - \sigma \mu_i^\theta$ ), and the difference of electrical potential ( ${}^b \phi - \sigma \phi$ ), but also an energetic contribution of the area and a degree of homogeneity  $p$  which is able to account for the behavior of the system when surfactant is added.

The total concentration of  $i$  can then be written:

$${}^m C_i = {}^b C_i (1 + x \varphi_i) \quad (13)$$

with

$$x = \frac{n_2 - {}^b n_2}{V} \quad (14)$$

For the equilibrium (1) of the addition of hydroxide ions to TNB, the apparent equilibrium constant, experimentally determined from the values of the total concentration in solution of AOH ( ${}^m C_{\text{AOH}}$ ), A ( ${}^m C_A$ ), and OH ( ${}^m C_{\text{OH}}$ ), is written:

$${}^m K = \frac{\{{}^m C_{\text{AOH}}\}}{\{{}^m C_A\} \{{}^m C_{\text{OH}}\}} \quad (15)$$

Taking into account the relation (13), this constant can be expressed as

$${}^m K = {}^b K \frac{1 + x \varphi_{\text{AOH}}}{(1 + x \varphi_A)(1 + x \varphi_{\text{OH}})} \quad (16)$$

where  ${}^b K$  is the apparent equilibrium constant associated with the volume component:

$${}^b K = \frac{\{{}^b C_{\text{AOH}}\}}{\{{}^b C_A\} \{{}^b C_{\text{OH}}\}} \quad (17)$$

We will assume that the  $\text{OH}^-$  ions, like the water, belong only to the volume component ( $x \varphi_{\text{OH}} = 0$ ), which implies

$${}^m K = {}^b K \frac{1 + x \varphi_{\text{AOH}}}{1 + x \varphi_A} \quad (18)$$

Then, the amount of micellized surfactant in solution ( $x$ ) intervenes in the expression for the apparent equilibrium constant.

**2. Kinetic Aspects.** We have decided to use, develop, and apply the approach of Marcelin–De Donder<sup>29</sup> to describe the kinetic aspects of the phenomenon. The rate of reaction can be expressed under the general form

$$v = {}^m \nu_0 \left[ \exp\left( \frac{\bar{A} - \bar{A}_{\text{eq}}}{RT} \right) - \exp\left( \frac{\bar{A} - \bar{A}_{\text{eq}}}{RT} \right) \right] \quad (19)$$

$\bar{A}$  and  $\bar{A}_{\text{eq}}$  are respectively the forward and reverse affinity and  $\bar{A}_{\text{eq}}$  and  $\bar{A}_{\text{eq}}$  the forward and reverse affinity at equilibrium. These parameters are identical in each point of the system when the only source of irreversibility is chemical. They are then independent of the localization of the species in the medium.  ${}^m \nu_0$  is the chemical exchange rate at equilibrium. This parameter describes the fact that the forward and reverse rates at equilibrium have a unique value,  ${}^m \nu_0$ . For a given value of equilibrium constant, we can suppose, as in electrochemistry, that the chemical systems are more or less fast.

For a given chemical reaction we can consider that the value of this chemical exchange rate depends on the dimension of the system within which it takes place. Indeed, the probability of collision will be assumed higher in the area content associated with dimension 2 than in a volume content associated with dimension 3.

We have shown that the experimental exchange rate  ${}^m \nu_0$  is linked to the exchange rates of the volume and area components, respectively  ${}^b \nu_0$  and  ${}^\sigma \nu_0$ , by



$${}^m\nu_0 = {}^b\nu_0 + x^\sigma\nu_0 \quad (20)$$

These relations allow us to link the forward and reverse rate constants to the coefficients  $\varphi_i$  of the different species and to  $x$  by

$${}^mk_1 = \frac{{}^bk_1 + x^\sigma k_1 \varphi_A \varphi_{OH}}{(1 + x\varphi_A)} \quad (21)$$

$${}^mk_{-1} = \frac{{}^bk_{-1} + x^\sigma k_{-1} \varphi_{AOH}}{(1 + x\varphi_{AOH})} \quad (22)$$

The ratio of these two constants gives the equilibrium constant (relation (18)).

The complete solution of the system implies the determination of the value of the retention coefficient of the activated complex  $T^*$ . Its value is linked to those of the exchange rates associated with the volume and the area by

$$\varphi_{T^*} = \frac{{}^\sigma\nu_0}{{}^b\nu_0} = \frac{{}^\sigma k_{-1}}{{}^b k_{-1}} \varphi_{AOH} \quad (23)$$

Its value is obtained by measurements of the solubility of TNB in various micellar solutions.

Moreover, we have shown in the previous paper<sup>17</sup> the relation between the values of  ${}^b\nu_0$  and the concentration of AOH at equilibrium:

$${}^b\nu_0 = {}^b k_{-1} {}^b C_{AOHeq} \quad (24)$$

The initial concentration of TNB introduced,  ${}^b C_A^\circ$ , is expressed by

$${}^b C_A^\circ = {}^b C_{Aeq} + {}^b C_{AOHeq} \quad (25)$$

The introduction of the equilibrium constant  ${}^b K$  leads to

$${}^b C_A^\circ = {}^b C_{AOHeq} \left( 1 + \frac{1}{{}^b K {}^b C_{OH}} \right) \quad (26)$$

The expression of  ${}^b\nu_0$  is then of the form

$${}^b\nu_0 = {}^b k_{-1} {}^b C_A^\circ {}^b K \frac{{}^b C_{OH}}{{}^b K {}^b C_{OH} + 1} \quad (27)$$

Thus, for a fixed initial concentration of TNB, the value of  ${}^b\nu_0$  depends solely on the amount of hydroxide ion introduced into solution. Its value is obtained in the premicellar medium.

Then, it is possible to determine independently the values of the exchange rates associated with the volume and the area using the relations (27) and (23).

## V. Exploitation of the Results

**1. Determination of the Retention Coefficients of TNB, the Monoadduct, and the Activated Complex.** The retention coefficients are determined from solubility measurements in micellar media. The solubility of TNB was measured in pure water, in the presence of 0.1 and 0.3 mol dm<sup>-3</sup> NaBr and in solutions of Brij 35 for the same salt concentrations at 298 K, below and above the cmc. According to the relation (13), the concentrations of TNB at saturation in micellar solutions are linked by

$${}^m C_{Asat} = {}^b C_{Asat} (1 + x\varphi_A) \quad (28)$$

Above the cmc, the solubility increases linearly with  $x$ . The values of  $\varphi_A$  obtained are listed in Table 2.

For both salt concentrations studied, the values of  $\varphi_A$  are independent of the amount of aggregated surfactant.

The values of the parameters  $\varphi_{AOH}$ ,  ${}^\sigma k_{-1}$ , and  $\varphi_{T^*}$  can be determined (relations (18), (22), and (23)) knowing the values of  $\varphi_A$ :

$$\varphi_{AOH} = \frac{1}{x} \left[ \frac{{}^m K}{{}^b K} (1 + x\varphi_A) - 1 \right] \quad (29)$$

$${}^\sigma k_{-1} = \frac{1}{x\varphi_{AOH}} [{}^mk_{-1}(1 + x\varphi_{AOH}) - {}^bk_{-1}] \quad (30)$$

$$\varphi_{T^*} = \frac{{}^\sigma k_{-1}}{{}^b k_{-1}} \varphi_{AOH}$$

These values are listed in Table 3a and discussed in the following paragraphs. For comparison, the values obtained with the surfactant DTABr are also reported for the same micellization conditions (same value of  $x$ , Table 3b).

**2. Kinetic Results for Brij 35 in 0.1 mol dm<sup>-3</sup> NaBr.** In Brij 35 micellar media in the presence of 0.1 mol dm<sup>-3</sup> NaBr, the values of  ${}^\sigma k_{-1}$  and all the values of the retention coefficients are independent of the amount of micellized amphiphile.

Thus, for this salt concentration, it appears that the area is a function of degree unity of the mass of surfactant ( $p = 1$ ). This implies that the pseudophase model can be used to describe the kinetic and thermodynamic behavior of this nucleophilic aromatic addition reaction. Similar behavior was described for cationic micelles of DTABr<sup>17</sup> for the same salt concentration. Under these conditions, the Brij 35 micellar media present a value of  $\varphi_{T^*}$  equal to 38 (Table 3). According to relation (23), this implies that the exchange rate associated with the area is 38 times higher than that associated with the volume. In the present case, the reaction in the area content is then faster than that in the volume content.

We can underline in this example that the phenomenon of “micellar catalysis” is the result of an increase of the value of the apparent exchange rate of the chemical reaction because of the introduction of a faster exchange rate associated with the area component. The system is then “faster” in the presence of surfactant, in the sense used in electrochemistry.

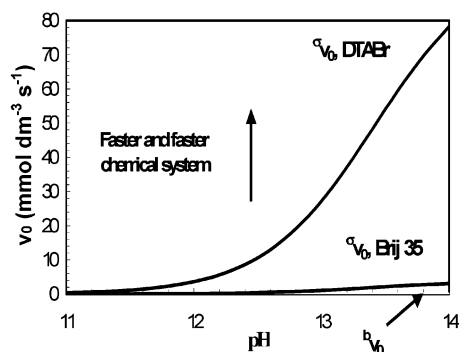
For example, in DTABr cationic micellar media, the values of the retention coefficients of all the negatively charged ionic species are higher than those obtained in neutral, nonionic media. This difference in behavior shows very different values of exchange rates associated with the area.

The ratio of the exchange rates associated with the area,  $\beta$ , which corresponds also to the ratio of the retention coefficients of the activated complex (relation (23)),

$$\beta = \frac{({}^\sigma\nu_0)_{DTABr}}{({}^\sigma\nu_0)_{Brij35}} = \frac{(\varphi_{T^*})_{DTABr}}{(\varphi_{T^*})_{Brij35}} \quad (31)$$

**TABLE 2: Values of Retention Coefficients of TNB,  $\varphi_A$ , at 298 K**

surfactant	Brij 35	
[NaBr] (mol dm <sup>-3</sup> )	0.1	0.3
$\varphi_A$ (dm <sup>3</sup> mol <sup>-1</sup> )	37 ± 6	21 ± 8



**Figure 3.** Evolution of  $v_0$  and  $b_0$  as a function of pH in Brij 35 and DTABr micellar media ( $[\text{NaBr}] = 0.1 \text{ mol dm}^{-3}$ ,  $p = 1$ ,  ${}^bC_A^\circ = 10^{-5} \text{ mol dm}^{-3}$ ).

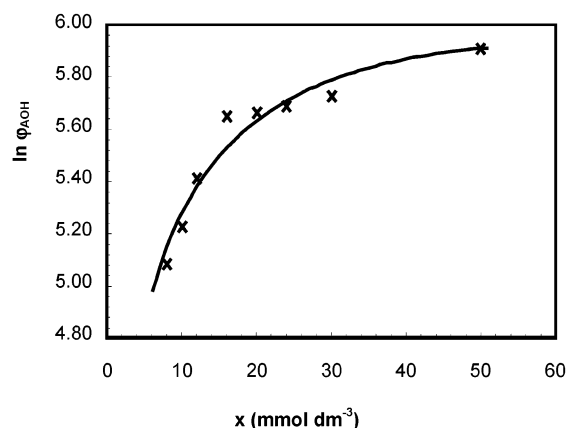
**TABLE 3: Values of  $\varphi_{\text{AOH}}$ ,  ${}^a k_{-1}$ , and  $\varphi_{\text{T}^*}$  in (a) Brij 35 and (b) DTABr at 298 K**

(a) In Brij 35			
$x$ (mmol dm <sup>-3</sup> )	$\varphi_{\text{AOH}}$ (dm <sup>3</sup> mol <sup>-1</sup> )	${}^a k_{-1}$ (s <sup>-1</sup> )	$\varphi_{\text{T}^*}$ (dm <sup>3</sup> mol <sup>-1</sup> )
In 0.1 mol dm <sup>-3</sup> NaBr			
7.9	273	1.43	40
9.9	266	1.35	37
15.9	263	1.35	36
19.9	303	1.35	42
23.9	295	1.25	36
29.9	299	1.20	37
49.9	326	1.09	36
In 0.3 mol dm <sup>-3</sup> NaBr			
8.0	161	1.39	23
10.0	186	1.51	29
12.0	224	1.59	36
16.0	284	1.72	50
20.0	288	1.56	46
24.0	295	1.49	45
30.0	307	1.41	44
50.0	368	1.26	47
(b) In DTABr			
$x$ (mmol dm <sup>-3</sup> )	$\varphi_{\text{AOH}}$ (dm <sup>3</sup> mol <sup>-1</sup> )	${}^a k_{-1}$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	$\varphi_{\text{T}^*}$ (dm <sup>3</sup> mol <sup>-1</sup> )
In 0.1 mol dm <sup>-3</sup> NaBr			
2.5	9505	1.04	1005
3.5	9965	0.97	990
5.5	10148	0.93	967
8.3	10743	0.89	977
13.1	12175	0.84	1049
15.5	11084	0.94	1062
In 0.3 mol dm <sup>-3</sup> NaBr			
5.7	2662	1.04	282.1
13.7	3470	1.00	353.6
21.7	4212	0.94	405.9
29.7	4649	0.92	434.6
37.7	4947	0.91	460.7
45.7	5257	0.89	479.0
53.7	5394	0.90	495.1
61.7	5605	0.89	511.5

is constant and equal to 27 for this concentration of salt. This implies that the exchange rate at equilibrium associated with the area in DTABr is equivalent to 27 times that in Brij 35 for a salt concentration of  $0.1 \text{ mol dm}^{-3}$ .

**3. Kinetic Results for Brij 35 in  $0.3 \text{ mol dm}^{-3}$  NaBr.** For this salt concentration, the values of Table 3 show that the values of the retention coefficient of the monoadduct,  $\varphi_{\text{AOH}}$ , vary with the amount of aggregated amphiphile, whereas those of TNB and the activated complex, respectively  $\varphi_{\text{A}}$  and  $\varphi_{\text{T}^*}$ , are constant.

When one of the retention coefficients varies, the pseudophase model cannot be adopted, and it must be considered that the



**Figure 4.** Variation of  $\ln \varphi_{\text{AOH}}$  as a function of  $x$  in Brij 35,  $[\text{NaBr}] = 0.3 \text{ mol dm}^{-3}$ . The curve was calculated according to the relation (32).

**TABLE 4: Parameters of Eq 32**

compound $i$	$\ln A$	$p - 1$	${}^a \gamma \alpha_i / RT$
AOH	8.98	0.75	7.78

area is not a function of degree unity of the amount of micellized surfactant.

We have previously shown<sup>17</sup> that the retention coefficient depends on the amount of aggregated amphiphile when the value of  $p$  differs from 1:

$$\ln \varphi_i = \ln A + (p - 1) \ln x - \frac{{}^a \gamma \alpha_i}{RT} x^{(p-1)} \quad (32)$$

where  $A$  is a constant and  $\alpha_i$  a specific coefficient of the variable of area of the solute  $i$ .

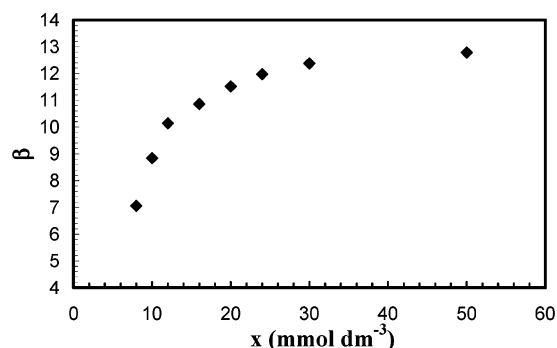
This relation embraces the special case when  $p = 1$ , where the retention coefficient is independent of  $x$ .

The least-squares method was used to analyze the experimental values and to determine the unknown parameters of this relation,  $A$ ,  $p$ , and  ${}^a \gamma \alpha_i$ . The results obtained for the monoadduct are listed in Table 4. Figure 4 shows the experimental data and the fit obtained.

The behavior of the system can be described by stating that the area is a homogeneous function of  $x$  of degree  $p = 1.75$ . The value of this degree of homogeneity is higher than unity. It implies that the area increases faster than the mass or that the system “creates some extra area” when the concentration of Brij 35 increases in the medium. The previous analysis poses a problem of coherence since the retention coefficients of TNB and  $\text{T}^*$  do not vary with  $x$ . Indeed, we could be tempted to conclude that  $p = 1$ . As for the previous study,<sup>17</sup> there are many pairs of values which lead to an almost total compensation of the terms with  $x$ . For example, consider the following parameter set:  $\ln A = 7.65$ ,  $p = 1.75$ , and  ${}^a \gamma \alpha_i / RT = 17.5$  for the activated complex, leading to a constant value of  $\varphi_{\text{T}^*}$  and  $\ln \varphi_{\text{T}^*} = 1.60$ . For the TNB with a similar parameter set ( $\ln A = 7.57$ ,  $p = 1.75$ , and  ${}^a \gamma \alpha_i / RT = 17.5$ ), we found that  $\varphi_{\text{A}}$  is constant and  $\ln \varphi_{\text{A}} = 1.32$ .

Similar behavior is found for DTABr ( $p = 1.38$ ) in salt solutions of NaBr with the same concentration.

It is then possible to compare the exchange rate associated with the area in Brij 35 solutions to the exchange rates associated with the area in DTABr solutions for this salt concentration. The values of the ratio  $\beta$  (relation (29)) are reported against the amount of aggregated surfactant,  $x$ , in Figure 5. This figure



**Figure 5.** Variation of  $\beta$  (relation (31)) as a function of  $x$  in  $[\text{NaBr}] = 0.3 \text{ mol dm}^{-3}$ .

shows that, for the range of concentration studied, the exchange rate associated with the area is much smaller in Brij 35 than in DTABr. The more the value of  $x$  increases, the greater is this effect. The value of this ratio is between 7 and 13. Then, the lower micellar reactivity corresponds to a medium where the exchange rate associated with the area is the lower. The system is then “faster” in the presence of DTABr than in Brij 35 for the range of amphiphile concentrations used.

## VI. Conclusions

In this paper, we have shown that a thermodynamic description of a micellar system can be obtained by introducing a variable of area into the expression for the internal energy. This variable is mainly thermodynamic and is not a measure of a specific surface. In the approach we propose, it is not necessary to consider the micelles as definite objects, which they are not.

The most important contribution we make to the description of the behavior of micellar solutions is no doubt to show that the rules of thermodynamics demand that a material content be associated with each variable having a dimension. When one introduces a variable of dimension 2, then one has to associate it with a content of the system, even if this is completely formal.

The content of the micellar solution is then separated in two components: one of volume associated with dimension 3 and one of area associated with dimension 2.

The volume is an extensive parameter: it is a homogeneous function of degree unity of its content. The area is not necessarily an extensive function: it does not necessarily vary linearly with its content. This approach is sufficient to describe the evolution of the behavior of micellar solutions when the concentration of surfactant increases.

The evolution of the shape of the micelles, the creation of new structures, can involve great modifications of the ratio between the content of area and its actual value.

For the case studied, we show for concentrations of  $0.1 \text{ mol dm}^{-3}$  NaBr that the variable of area varies linearly with the concentration of neutral amphiphile, whereas for a more concentrated salt solution, the area varies as the power 1.75 of its concentration. In this last case, when the amount of surfactant in solution increases, then some extra area is created. This phenomenon has been previously shown to occur in the behavior of cationic surfactants such as DTABr.

Another point which seems important in our analysis is the notion of “micellar catalysis” in terms of increase of the exchange rate at equilibrium for the reaction considered. The formal separation of the content of the solution into two components, associated with different dimensions, naturally leads us to suppose that the probability of collision between reactants is different in the two regimes. Thus, the exchange

rates at equilibrium must be different. The analysis of the experimental data confirms this fact: in the case of neutral surfactants, the exchange rate associated with the content of dimension 2 equals 40 times the one associated with the content of dimension 3. It is certain that the difference of rate depends also on other parameters linked to the differences in environment, mainly on the electrical charge of the amphiphiles.

When the exchange rates in the area content for the aggregates of the cationic and neutral surfactant are compared, we can see that the exchange rate for the charged amphiphiles is 27 times that for the neutral surfactant. As shown here, this is the result of greater stabilization of the activated complex in the area content when the amphiphiles are charged.

That “slow” chemical systems become “fast” in the presence of a catalyst is a common idea in electrochemistry. In the sense used here, micellar catalysis is another such phenomenon.

## VII. Glossary

$^bX$  = variable relative to the volume

$^mX$  = variable relative to the micellar medium

$^aX$  = variable relative to the area

$G$  = Gibbs energy or free enthalpy

$\mu_i$  = chemical potential of the solute  $i$

$\mu_i^\theta$  = standard chemical potential of the solute  $i$  in solution, referring to the behavior of the diluted solutions for the molar scale

$x$  = total concentration of surfactant aggregated in solution

$\{C_i\}$  = value of the molar concentration of  $i$

$K$  = equilibrium constant

$k$  = observed rate constant of the reaction

$k_1$  and  $k_{-1}$  = forward and reverse rate constants

$n_i$  = number of moles of  $i$

$V$  = total volume

$^aA_i'$  = partial area of  $i$

$\phi$  = electrical potential

$^a\gamma$  = interfacial tension

eq = “at equilibrium”

$\bar{A}$  and  $\bar{A}$  = “forward” and “reverse” affinities

$\nu$  = molar rate of reaction

$\nu_0$  = chemical exchange rate at equilibrium

$\varphi_i$  = retention coefficient of  $i$

$^aX_i$  = molar micellar ratio of  $i$

$p$  = degree of homogeneity of the area

$z_i$  = charge of ion  $i$

$F$  = Faraday constant

$C_i^\circ$  = total concentration of  $i$

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