Kinetic Study of Ni^{2+} and Co^{2+} Complexation by PADA in AOT-Based Water-in-Oil Microemulsions

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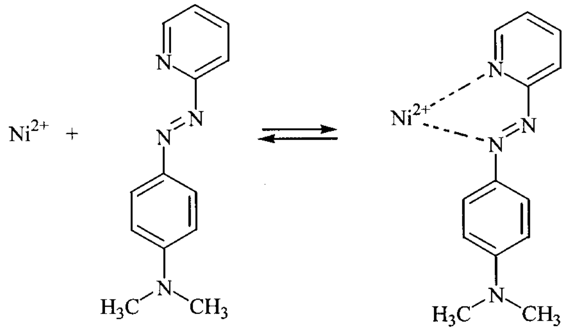
A kinetic study was carried out into the complexation of Ni^{2+} and Co^{2+} with the bidentate ligand pyridine-2-azo-*p*′-(*N*,*N*-dimethylaniline) (PADA) in AOT/isooctane/water microemulsions [where AOT = sodium bis(2-ethylhexyl)sulfosuccinate]. The results obtained show that the macroscopic rate constants for the formation of the Ni^{2+}-PADA and Co^{2+}-PADA complexes decrease as the surfactant concentration and the water content of the system increase. The rate constants are in all cases greater than those observed in an aqueous medium, with catalytic effects of up to 25 times. To interpret the kinetic results a model has been proposed which considers the distribution of PADA between the continuous medium and the interface of the microemulsion, and the distribution of the Ni^{2+} and the Co^{2+} cations between the aqueous microdroplet and the interface. The formation and dissociation reactions of the complexes take place only at the interface. On the basis of the model we obtained values for the rate constants for the formation, k_1^i, and decomposition, k_{-1}^i, of the complexes for various values of W (W = $[H_2O]/[AOT]$). The results show that k_{-1}^i is independent of the composition of the microemulsion and that k_1^i increases as W decreases. The results also show that the rate constants for the formation of the Co^{2+}-PADA complex are approximately 50 times greater than those of the Ni^{2+}-PADA complex. These results are compatible with the fact that the reaction follows an Eigen–Wilkins-type mechanism and that, in the presence of added salt, there is an increase in the rate constant of water exchange as the saline content of the microdroplet increases, that is, as W decreases.

Introduction

Microemulsions are thermodynamically stable dispersions of either water-in-oil (w/o) or oil-in-water (o/w), their stability resulting from the presence of a suitable surfactant. Microemulsion droplets are spherical droplets of water or oil coated with a monolayer of surfactant dispersed in the continuous phase and have small radii in the range 0–50 nm. Microemulsions are macroscopically homogeneous but microscopically heterogeneous owing to the amphiphilic nature of the surfactant that resides in the interface between water and the nonpolar solvent. The solutes can be located in three different compartments: (i) the internal aqueous core or water pool, (ii) the micellar interface formed by a monolayer of surfactant molecules with their polar head groups oriented toward the water pool, and (iii) the external organic phase.[1–4]

The transition from a homogeneous solvent system to a microemulsion may affect not only the rate of reactions but also the regioselectivity of organic reactions[5] due to the orientation of reactants at the oil/water interface and even the mechanism by which the reaction occurs.[6] Previously we investigated the effect of the composition of the microemulsion on the equilibrium constant for the formation of the complexes of metallic cations with the bidentate ligand pyridine-2-azo-*p*′-(*N*,*N*-dimethylaniline) (PADA), that is, Ni^{2+}-PADA and Co^{2+}-PADA[7] (Scheme 1). The results obtained show that the complexation constants for the complexes formed in the interface are lower than the values observed for complexation in an aqueous medium and that they decrease as the water content of the microemulsion increases as a consequence of the greater solvation of the Ni^{2+} and Co^{2+} cations in the interface of the microemulsion compared with in the aqueous medium. However, as the water content decreases less water will be available for sol-



PADA

Scheme 1

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vation and consequently the capacity for complexation will increase.

A number of kinetic studies involving metal-ion complexation with bidentate ligand pyridine-2-azo-*p*′-(*N*,*N*-dimethylaniline) in bulk and in dispersed media have been carried out. The reaction rate was observed to be metal-ion-dependent in water (bulk and dispersed),[8] dimethyl sulfoxide,[9] dimethylformamide,[9] and dispersed glycerol,[10] but metal-ion-independent in bulk glycerol.[11]

In this article, the effect of the composition of the microemulsion on the complexation of a metallic cation, Ni^{2+}, by a bidentate ligand, pyridine-2-azo-*p*′-(*N*,*N*-dimethylaniline) (PADA), in microemulsions of sodium bis(2-ethylhexyl)sulfosuccinate (AOT)/isooctane/water at 25°C will be examined. The study had various aims, namely to develop a kinetic model applicable to the study of reversible reactions and to investigate whether the changes in the water properties of the microemulsion have consequences for the complexation of the Ni^{2+} cation by the bidentate ligand. For the purposes of comparison, a more limited kinetic study has been carried out on the formation of the Co^{2+}-PADA complex in order to determine the differences between the water-exchange constants in $(H_2O)_6Ni^{2+}$ and $(H_2O)_6Co^{2+}$.

Results

Owing to the reversible nature of the complexation reaction of Ni^{2+} with PADA, we have carried out experiments in which the Ni^{2+} concentration was varied while keeping the composition of the microemulsion and the concentration of the ligand constant. In all cases the rate constant observed, k_{obs}, varies linearly with $[Ni^{2+}]_T$. From this linear dependence we can obtain the apparent values of the rate constants for complex formation, k_1^{app}, and decomposition, k_{-1}^{app}, for each microemulsion composition [Equation (1)].

$$Ni^{2+} + PADA \underset{k_{-1}^{app}}{\overset{k_1^{app}}{\rightleftharpoons}} Ni^{2+}\text{-PADA}$$

$$k_{obs} = k_1^{app}\left[Ni^{2+}\right]_T + k_{-1}^{app} \qquad (1)$$

To study the effect of the microemulsion composition on the rate constants k_1^{app} and k_{-1}^{app} we carried out two types of experiments: variation of the concentration of the surfactant with *W* (*W* = $[H_2O]/[AOT]$) kept constant, and variation of *W* with the surfactant concentration kept constant.

Effect of Surfactant Concentration

Figure 1 shows the effect of Ni^{2+} concentration on k_{obs} for microemulsions of *W* = 11.1, where the surfactant concentration referred to the total volume of the system varies between 0.100 and 0.667 M. We can see that as the surfactant concentration increases the slope decreases while the ordinate remains practically constant. Table 1 shows the values of k_1^{app} and k_{-1}^{app}, as obtained with Equation (1). The value of k_1^{app} in all cases is greater than that obtained in an aqueous medium, $k_1^{H_2O}$ = (1010 ± 30) $M^{-1}\,s^{-1}$. Note that a catalytic effect of more than 27 times can be observed. The value of k_{-1}^{app} is practically independent of the surfactant concentration and is also greater than the value obtained in an aqueous medium. Errors in determining k_{-1}^{app} are very large and sometimes are higher than the value of the rate constant. However, as will be shown later the agreement between the kinetic and thermodynamic equilibrium constant is a good test of the reliability of the kinetic model. Because of the large errors in determining k_{-1}^{app}, for further comparisons we have calculated k_{-1}^{app} from the thermodynamic equilibrium constant and the k_1^i values.

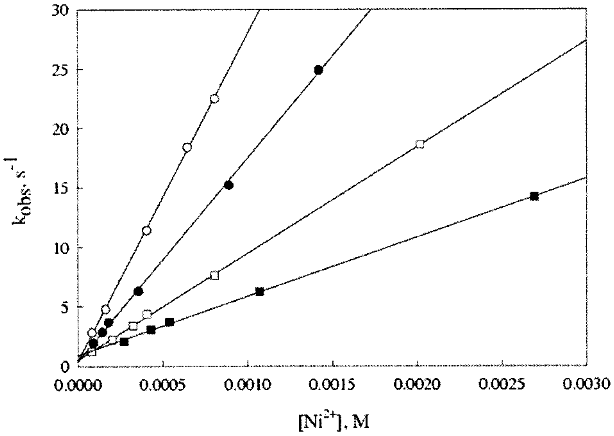


Figure 1. Effect of $[Ni^{2+}]$ on k_{obs} in the complexation of Ni^{2+} with PADA in microemulsions of AOT/isooctane/water of *W* = 11.1 at 25 °C: (○) [AOT] = 0.100 M; (●) [AOT] = 0.222 M; (□) [AOT] = 0.500 M; (■) [AOT] = 0.667 M

Table 1. Values[a] of k_1^{app} and k_{-1}^{app} obtained for the complexation of Ni^{2+}-PADA in microemulsions of *W* = 11.1 and different concentrations of surfactant, in accordance with Equation (1), and in pure water

[AOT]/M	Z[b]	k_1^{app}/$M^{-1}\,s^{-1}$	k_{-1}^{app}/s^{-1}
0.100	57.07	27 500 ± 320	0.45 ± 0.16
0.120	46.97	25 040 ± 210	0.66 ± 0.12
0.160	34.35	23 020 ± 360	0.43 ± 0.20
0.220	24.02	17 060 ± 220	0.41 ± 0.15
0.333	14.68	13 240 ± 210	0.44 ± 0.14
0.500	8.60	8930 ± 80	0.52 ± 0.73
0.667	6.58	7275 ± 70	0.91 ± 0.10
bulk water		1010 ± 30	0.18 ± 0.02

[a] ± is the standard deviation obtained from the plot. [b] *Z* = [isooctane]/[AOT].

Effect of the Water Content of the System

Experiments have also been carried out in which values of k_{obs} were determined at various Ni^{2+} concentrations by using microemulsions in which the surfactant concentration was kept constant, [AOT] = 0.333 M, and the molar relation, *W*, varies from *W* = 2 to 45. Figure 2 shows the data obtained for values of *W* = 2, 9 and 45. The gradient of the slope decreases with increasing water content in the system, while the ordinate remains practically constant. Table 2 shows the values of k_1^{app} and k_{-1}^{app}, as obtained from Equation (1). The k_1^{app} values are in all cases higher than the value obtained in pure water and decrease as the water content of the system increases. A maximum catalytic effect of approximately 20 times was observed for *W* = 2. The values of k_{-1}^{app} are practically independent of the microemulsion composition and greater than the value obtained in pure water.

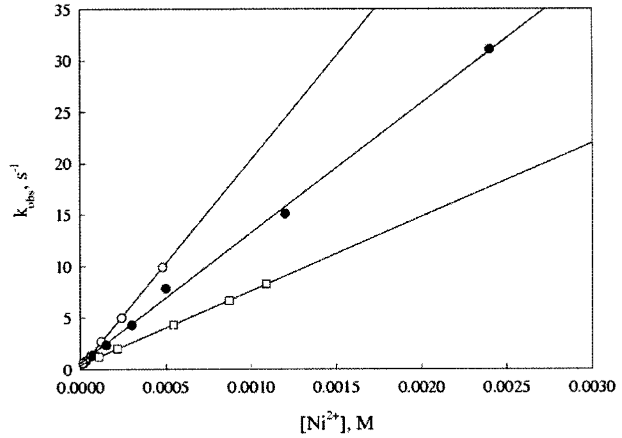


Figure 2. Effect of [Ni^{2+}] on k_{obs} in the complexation of Ni^{2+} with PADA in microemulsions of AOT/isooctane/water, where [AOT] = 0.333 M at 25 °C: (○) *W* = 2; (●) *W* = 9; (□) *W* = 45

Table 2. Values[a] of k_1^{app} and k_{-1}^{app} for Ni^{2+}-PADA complexation in microemulsions of [AOT] = 0.333 M and with different values of *W*, in accordance with Equation (1), and in pure water

W	*Z*[b]	k_1^{app}/M^{-1} s^{-1}	k_{-1}^{app}/s^{-1}
2	15.69	20 152 ± 216	0.21 ± 0.05
3	15.59	17 449 ± 163	0.34 ± 0.13
5	15.83	14 969 ± 125	0.54 ± 0.07
7	15.13	13 856 ± 146	0.42 ± 0.10
9	14.90	12 709 ± 149	0.34 ± 0.17
10.5	14.74	12 262 ± 72	0.44 ± 0.11
11.1	14.68	13 242 ± 208	0.44 ± 0.14
15	14.25	11 043 ± 125	0.54 ± 0.11
20	13.71	8670 ± 33	0.38 ± 0.07
25	13.16	4869 ± 48	0.66 ± 0.27
30	12.61	3828 ± 90	0.21 ± 0.37
35	12.07	6999 ± 154	0.54 ± 0.18
40	11.52	3391 ± 104	0.27 ± 0.29
45	10.98	7180 ± 90	0.43 ± 0.16
bulk water		1010 ± 30	0.18 ± 0.02

[a] ± is the standard deviation obtained from the plot. [b] *Z* = [isooctane]/[AOT].

Formation of the Co^{2+}-PADA Complex

The rate constants for the formation of the Co^{2+} complexes are much greater than those for the formation of the Ni^{2+} complexes. For this part of the study we carried out a very limited number of experiments by using only one Co^{2+} concentration. The obtention of the results, which are shown in Table 3, was limited because the rate of the reaction is close to the stopped-flow detection limit, which meant that high concentrations of Co^{2+} could not be used. Likewise the use of small concentrations of Co^{2+} necessitates the use of concentrations of PADA in the vicinity of 1×10^{-6} M in order to guarantee pseudo-first-order conditions, which brings about a very small variations in absorbance. The kinetic results obtained for the formation of the Co^{2+}-PADA complex will be compared with those of Ni^{2+}-PADA and related to its rate of water exchange.

Table 3. Values of k_{obs} obtained for the formation of the Co^{2+}-PADA complex[a] in microemulsions of AOT/isooctane/water at 25 °C

W	*Z*[b]	[AOT]/M	[Co^{2+}]/M	k_{obs}/s^{-1}
2	15.7	0.333	1.50×10^{-5}	171
3	15.6	0.333	2.25×10^{-5}	164
5	15.8	0.333	3.75×10^{-5}	201
8	15.0	0.333	6.00×10^{-5}	224
10	14.8	0.333	7.50×10^{-5}	247
13	14.5	0.333	9.75×10^{-5}	245
17	56.4	0.100	3.75×10^{-5}	268
17	32.3	0.166	6.37×10^{-5}	250
17	23.4	0.222	8.37×10^{-5}	270
17	12.9	0.333	1.25×10^{-4}	278
17	7.96	0.500	1.91×10^{-4}	275
17	4.94	0.667	2.55×10^{-4}	263
20	13.7	0.333	1.50×10^{-4}	278
35	12.1	0.333	2.62×10^{-4}	302
45	11.0	0.333	3.37×10^{-4}	306

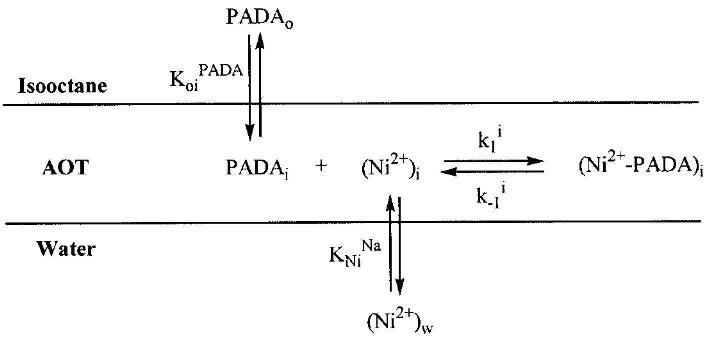
[a] The concentrations given refer to the total volume of the system: $[PADA]_T = 3.5 \times 10^{-6}$ M. [b] *Z* = [isooctane]/[AOT].

Discussion

In order to carry out a quantitative interpretation of the results obtained it is necessary to take into account the distribution and compartmentalization of the reagents between the dispersed water droplets, the continuous oil phase, and the amphiphilic film of the microemulsion. In this way we should obtain the true rate constants in the phase in which the reaction takes place. Previous studies on PADA distribution in AOT-based microemulsions showed that PADA is distributed only between the continuous oil phase and the interface of the system.[7]

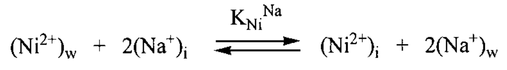
Derivation of the Kinetic Parameters

To obtain the true rate constants it is necessary to propose a reaction mechanism. This must be similar to that obtained previously when studying the effect of the microemulsion composition on the equilibrium constant. Therefore we propose the reaction model shown in Scheme 2, where the subscripts o, i, and w refer to the oil, interface, and water pseudophases of the system, respectively.



Scheme 2

PADA distribution between the continuous medium and the interface of the microemulsion is governed by the following equilibrium constant: $K_{oi}^{PADA} = ([PADA]_i/[PADA]_o)\,Z$, where oi indicates that the equilibrium constant refers to the incorporation of PADA in the interface from the oil and Z is the molar ratio, Z = [isooctane]/[surfactant]. The reagent ions, Ni^{2+}, are distributed between the aqueous microdroplets and the interface of the microemulsion. Their distribution will be governed by an ionic exchange equilibrium (Scheme 3).



$$(Ni^{2+})_w + 2(Na^+)_i \overset{K_{Ni}^{Na}}{\rightleftharpoons} (Ni^{2+})_i + 2(Na^+)_w$$

Scheme 3

The reaction will take place only at the interface of the microemulsion, where k_1^i and k_{-1}^i are the rate constants for the formation and dissociation of the complex in the volume of the interface. If we consider a balance of matter for the total PADA concentration and the distribution constant for PADA between the pseudophases of the microemulsion we have Equation (2<frr2>):

$$[PADA]_T = [PADA]_i\left(\frac{K_{oi}^{PADA} + Z}{K_{oi}^{PADA}}\right) + [Ni^{2+} - PADA]_i \tag{2}$$

whence we obtain the following expression for the observed rate constant:

$$k_{obs} = k_1^i [Ni^{2+}]_i^i \frac{K_{oi}^{PADA}}{K_{oi}^{PADA} + Z} + k_{-1}^i \tag{3}$$

where $[Ni^{2+}]_i^i$ is the concentration of Ni^{2+} at the interface referred to the volume of the interface of the microemulsion. To be able to make use of Equation (3) we should express it according to the total Ni^{2+} concentration referred to the total volume of the system, $[Ni^{2+}]_i$. If we take the volume of the interface to be the same as the volume occupied by the surfactant, as is usual in simple micellar systems,[12] we can rewrite Equation (3) as Equation (4):

$$k_{obs} = k_1^i \frac{[Ni^{2+}]_i}{\bar{V}_{AOT}\,[AOT]} \frac{K_{oi}^{PADA}}{K_{oi}^{PADA} + Z} + k_{-1}^i \tag{4}$$

where $[Ni^{2+}]_i$ represents the total Ni^{2+} concentration in the interface referred to the total volume of the system and $\bar{V}_{AOT}$ is the molar volume of the AOT molecule. To evaluate $[Ni^{2+}]_i$ we need to look to the ionic exchange (Scheme 3), and define the exchange equilibrium constant between Na^+ and Ni^{2+} as Equation (5):

$$K_{Ni}^{Na} = \frac{[Ni^{2+}]_i^i}{[Ni^{2+}]_w^w}\left(\frac{[Na^+]_w^w}{[Na^+]_i^i}\right)^2 \tag{5}$$

where the concentrations in the interface and the water refer, respectively, to the volumes of the interface and the water. These concentrations, again, refer to the total volume of the system by just considering the volumes of the interface and aqueous microdroplets; thus the ionic exchange equilibrium constant can be rewritten as Equation (6),

$$K_{Ni}^{Na} = \frac{[Ni^{2+}]_i}{[Ni^{2+}]_w}\left(\frac{[Na^+]_w}{[Na^+]_i}\right)^2 \frac{\bar{V}_{AOT}\,[AOT]}{\bar{V}_{H_2O}\,[H_2O]} \tag{6}$$

where $\bar{V}_{H2O}$ refers to the water molar volume.

By making use of the methodology devised to study the effect of the composition of the microemulsion on the complexation constant,[7] we can obtain the following expression for $[Ni^{2+}]_i$ [Equation (7)],

$$[Ni^{2+}]_i = [Ni^{2+}]_T \frac{K_{Ni}^{Na}\,\beta^2 W}{(1-\beta)^2\,18.9 + K_{Ni}^{Na}\,\beta^2 W} \tag{7}$$

where β is the fraction of neutralized charge at the interface of the microemulsion. By using values of $\bar{V}_{AOT} = 0.37\ \text{M}^{-1}$, $\beta = 0.8$ and $K_{Ni}^{Na} = 43$, we can make the following approximation [Equation (8)]:

$$\frac{(1-\beta)^2 18.9 + K_{\mathrm{Ni}}^{\mathrm{Na}}\beta^2 W}{K_{\mathrm{Ni}}^{\mathrm{Na}}\beta^2 W} = \frac{0.756 + 27.5W}{27.5W} \approx 1 \tag{8}$$

Hence we find that $[\mathrm{Ni}^{2+}]_{\mathrm{i}} = [\mathrm{Ni}^{2+}]_{\mathrm{T}}$, which enables us to rewrite Equation (4) as Equation (9):

$$k_{obs} = k_1^i \frac{K_{\mathrm{oi}}^{\mathrm{PADA}}}{K_{\mathrm{oi}}^{\mathrm{PADA}} + Z}\,\frac{[\mathrm{Ni}^{2+}]_T}{\bar{V}_{\mathrm{AOT}}\,[\mathrm{AOT}]} + k_{-1}^i \tag{9}$$

whence we obtain the following expressions [Equation (10) and Equation (11)] which relate k_1^{app} and k_{-1}^{app} to the true rate constants in the interface and parameter Z of the composition of the microemulsion.

$$k_1^{app} = k_1^i \frac{K_{\mathrm{oi}}^{\mathrm{PADA}}}{K_{\mathrm{oi}}^{\mathrm{PADA}} + Z}\,\frac{1}{\bar{V}_{\mathrm{AOT}}[\mathrm{AOT}]} \tag{10}$$

$$k_{-1}^{app} = k_{-1}^i \tag{11}$$

Equation (10) can be rearranged to Equation (12).

$$\frac{1}{k_1^{\mathrm{app}}\,\bar{V}_{\mathrm{AOT}}\,[\mathrm{AOT}]} = \frac{1}{k_1^i} + \frac{1}{K_{\mathrm{oi}}^{\mathrm{PADA}} k_1^i} Z \tag{12}$$

Figure 3 shows a good linear dependence between $1/(k_1^{\mathrm{app}} 0.37[\mathrm{AOT}])$ or $1/(k_1^{\mathrm{app}}\bar{V}_{\mathrm{AOT}}[\mathrm{AOT}])$ and the Z parameter of microemulsion composition for experiments carried out at $W = 11.1$. The fulfillment of Equation (12) proves the validity of the model proposed to explain the experimental behavior observed when studying the formation of the Ni^{2+}-PADA complex in microemulsions of AOT/isooctane/water. From the values of the ordinate and the slope of Figure 3 we can obtain values for the formation constant of the complex in the interface and of the distribution constant of PADA between the continuous medium and the interface of the microemulsion. The value of $K_{\mathrm{oi}}^{\mathrm{PADA}} = 84$ concurs well with that obtained previously.[7] The value obtained for the true rate constant in the interface, $k_1^{\mathrm{i}} = (1950 \pm 120)\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$, at $W = 11.1$ is slightly greater than the value obtained in pure water.

As we can see in Table 1 the value of k_{-1}^{app} is practically independent of the AOT concentration for experiments carried out at $W = 11.1$. Therefore we can conclude that k_{-1}^{i} is independent of the AOT concentration. By using a mean value[13] of $k_{-1}^{\mathrm{i}} = 0.48\ \mathrm{s}^{-1}$ we can obtain the value for the equilibrium constant for the formation of the Ni^{2+}-PADA complex: $K_{\mathrm{kinetic}} = k_1^{\mathrm{i}}/k_{-1}^{\mathrm{i}}$. The value obtained, $K_{\mathrm{kinetic}} = (4060 \pm 280)\ \mathrm{M}^{-1}$ concurs with the thermodynamic value determined previously,[7] $K_{\mathrm{thermodynamic}} = (4600 \pm 230)\ \mathrm{M}^{-1}$. The fulfillment of Equation (12) and the values obtained for $K_{\mathrm{oi}}^{\mathrm{PADA}}$ and K_{kinetic} are good evidence of the validity of the proposed model.

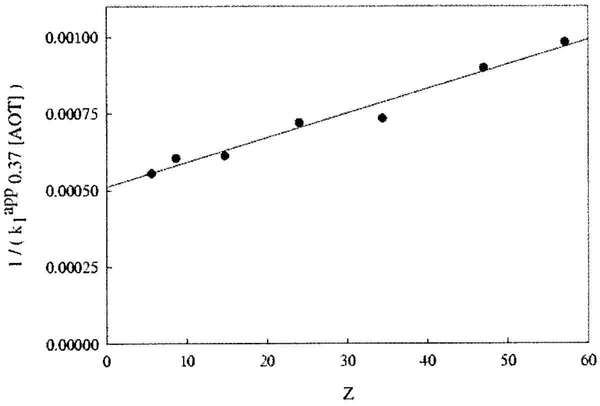


Figure 3. Variation of $1/k_1^{\mathrm{app}}[\mathrm{AOT}]$) [with the parameter Z of composition of the microemulsion in accordance with Equation (12), data in Table 1]; experiments were carried out at $W = 11.1$ and 25 °C

On the basis of Equation (12) and the values of k_1^{app} in Table 2 we can obtain a value of k_1^{i} for each W value. Figure 4 shows the values obtained, as well as the value obtained in an aqueous medium. As we can see k_1^{i} increases as the water content of the microemulsion decreases. This behavior is not predicted by Equation (12) which considers k_1^{i} to be independent of W. The values of k_1^{i} vary with W as a result of changes in the properties of the interfacial water, as has also been shown in studies involving solvolysis reactions.[14]

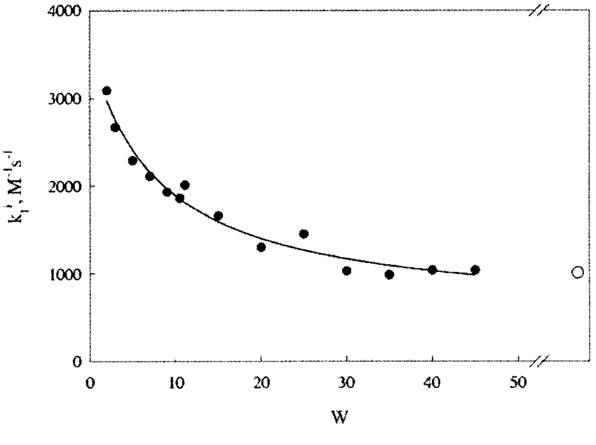


Figure 4. Effect of W on the values of k_1^{i} for the formation of the Ni^{2+}-PADA complex in the interface of a microemulsion of AOT/isooctane/water at 25 °C (●) and in pure water (○)

Table 2 shows the values of k_{-1}^{app} which allow us to obtain values of k_{-1}^{i} in accordance with Equation (11). However the uncertainty involved in determining the ordinates in experiments, such as those shown in Figures 1 and 2, means that the values of k_{-1}^{app} have an error margin which is sometimes greater than the actual value of the ordinate. Therefore, we decided to obtain the value of k_{-1}^{i} by comparing the kinetic and thermodynamic data as follows: $k_{-1}^{\mathrm{i}} = k_1^{\mathrm{i}}/K$, using the values of the equilibrium constant for the formation of the Ni^{2+}-PADA complex determined previously.[7] The values obtained for k^{i}_{-1} are approximately independent of the composition of the microemulsion and in all cases they are slightly greater than the value obtained in pure water (Figure 5).

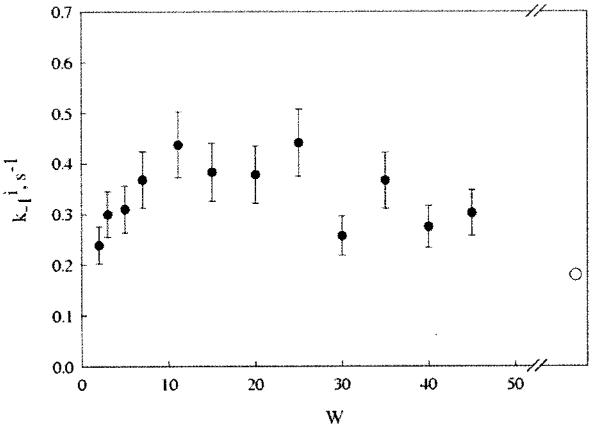


Figure 5. Effect of W on the values of k^{i}_{-1} for the dissociation of the Ni^{2+}-PADA complex in the interface of a microemulsion of AOT/isooctane/water at 25 °C (●) and in pure water (○)

Formation of the Co^{2+}-PADA Complex

Once the validity of the kinetic model developed for the formation of the Ni^{2+}-PADA complex has been verified, this formalism can be applied to the analysis of the data obtained for the Co^{2+}-PADA complex. On the basis of Equation (9), and by taking into account the expression $K = k^{i}_{1}/k^{i}_{-1}$, we can write Equation (13).

$$k_{obs} = k_1^{i} \frac{K_{oi}^{PADA}}{K_{oi}^{PADA} + Z} \frac{[Co^{2+}]_T}{\bar{V}_{AOT}\,[AOT]} + \frac{k_1^{i}}{K} \tag{13}$$

By applying Equation (13) to the data in Table 3 we can obtain values of k^{i}_{1} and k^{i}_{-1} for each composition of the microemulsion by using the value of $K_{oi}^{PADA} = 99$ obtained previously.[7] From the experiments carried out at $W = 17$ and by using the value of $K = 372$ we can obtain the values of k^{i}_{1} and k^{i}_{-1} for each AOT concentration. The results obtained, $k^{i}_{1} = (7.6 \pm 0.4) \times 10^{4}\ M^{-1}\ s^{-1}$ and $k^{i}_{-1} = (203 \pm 9)\ s^{-1}$ show that k^{i}_{1} is very near to the value obtained in pure water,[8c] $k_1^{water} = 7.6 \times 10^{4}\ M^{-1}\ s^{-1}$, as noted also for the Ni^{2+}-PADA complexes. However, the value of k^{i}_{-1} is much greater than that obtained in pure water, $k_1^{water} = 36\ s^{-1}$. This difference in behavior is a consequence of the differences between the stability constants of the Ni^{2+}-PADA and Co^{2+}-PADA complexes in the microemulsions and in pure water.

From the experimental results shown in Table 3 and the values of K_{oi}^{PADA} and the equilibrium constant for the formation of the Co^{2+}-PADA complex we can calculate the values of the rate constants for the formation, k^{i}_{1}, and dissociation, k^{i}_{-1}, of the complex in the interface for different W values. Figure 6 and Figure 7 show the variation of k^{i}_{1} and k^{i}_{-1} with W; behavior parallel to that observed for the formation of the Ni^{2+}-PADA complexes is shown.

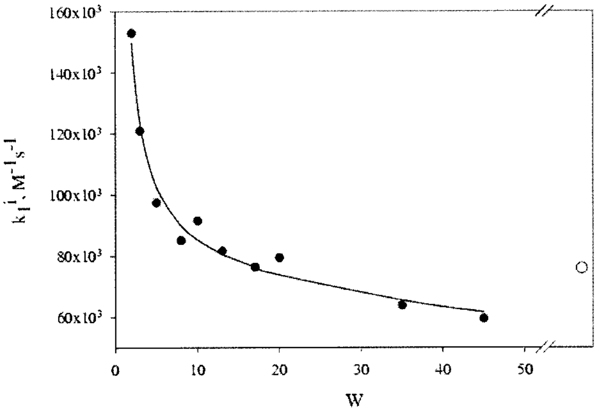


Figure 6. Effect of W on the values of k^{i}_{1} for the formation of the Co^{2+}-PADA complex in the interface of a microemulsion of AOT/isooctane/water at 25 °C (●) and in pure water (○)

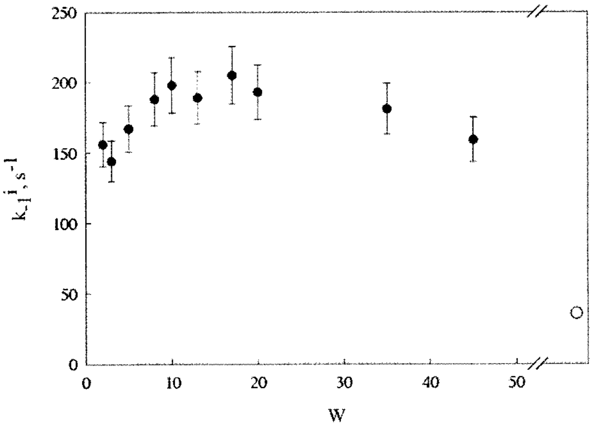


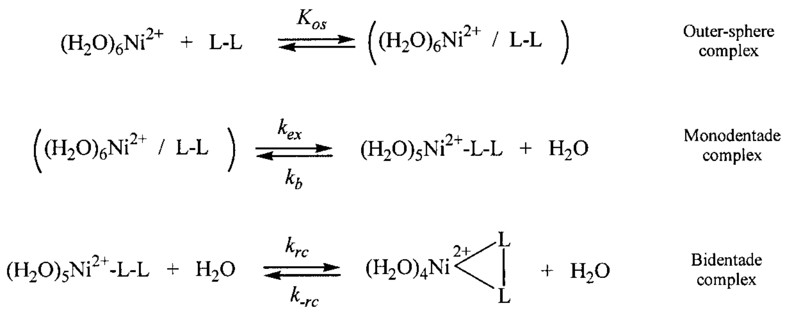
Figure 7. Effect of W on the values of k^{i}_{-1} for the dissociation of the Co^{2+}-PADA complex in the interface of a microemulsion of AOT/isooctane/water at 25 °C (●) and in pure water (○)

Reaction Mechanism

As we can see in Figure 4 the rate constant for the formation of the Ni^{2+}-PADA complex increases as the water content of the microemulsion decreases, while the rate constant for the dissociation of the complex remains practically the same (Figure 5). To interpret these results kinetically it is necessary to consider the mechanism for the formation of the Ni^{2+}-PADA complex.

The coordination of a ligand molecule such as PADA to an hexasolvated transition-metal ion is usually assumed to follow an interchange mechanism[15] of the Eigen–Wilkins type.[16] The reaction pathway can be broken down into successive steps (Scheme 4).

An outer-sphere complex is formed between the hydrated metal ion and the ligand, and then the ligand replaces a water molecule in the inner coordination sphere. For most labile metals, including Ni^{2+}, the second step is rate-de-



Scheme 4

termining and the observed second-order rate constant, k_1, is equal to $K_{os}k_{ex}$, where K_{os} is the stability constant of the outer-sphere complex and k_{ex} is the first-order rate constant for water exchange at the metal ion. When the incoming ligand is bidentate, a ring-closure step must be added. If a steady-state approximation is applied to the formation of the monodentate complex, the observed rate constants for the formation and dissociation of the bidentate complex are given by Equation (14) and Equation (15),

$$k_1 = \frac{K_{os}k_{ex}k_{rc}}{(k_b + k_{rc})} \tag{14}$$

$$k_{-1} = \frac{k_b k_{-rc}}{(k_b + k_{rc})} \tag{15}$$

where k_{rc} is the rate constant for ring closure and k_b is the rate constant for dissociation of the monodentate intermediate.

If ring-closure is fast compared with dissociation of the monodentate intermediate ($k_{rc} >> k_b$) then these expressions can be reduced to $k_1 = K_{os}k_{ex}$ and $k_{-1} = k_b k_{-rc}/k_{rc}$, and the kinetics of formation of the chelate are identical to those observed with a monodentate ligand. In the reaction of PADA with Ni^{2+} the replacement of the first water molecule in the inner coordination sphere is the rate-determining step.

The results obtained (Figure 4) indicate that the rate constant for the formation of the Ni^{2+}-PADA complex in the interface of the microemulsion increases as the water content of the microemulsion decreases and in all cases it is greater than the value observed in an aqueous medium. At first view one would expect the change in the rate constants to be related to the changes in the structural properties of the water as *W* decreases; as *W* decreases the interactions between the interfacial water and the head groups of the surfactant increase. As we have commented previously,[7] in the AOT-based microemulsions the interaction of the water with the surfactant's SO_3^- group causes an increase in the electron density of the oxygen atoms of the water molecules in such a way that their nucleophilicity increases. These changes in the nucleophilic character of the interfacial water are shown when we study solvolysis reactions which have a strong associative character, for example, the solvolysis of benzoyl chlorides substituted with electron-attracting groups. In these cases the rate constant for the reaction in the interface also increases as *W* decreases.

The experimental results show that k_1^i, where $k_1 = K_{os}k_{ex}$, increases as the water content of the system decreases. This must be a consequence of the decrease in water available for solvation. When $W = 10$, 10 water molecules exist for each surfactant molecule. Clearly this is insufficient for solvation, hence the Ni^{2+} cation which is added to the system will not have six water molecules for its hydration. Hence the lack of hydration will be the reason for the increase in the water-exchange rate constant, k_{ex}.

Hubbard and co-workers[17] have studied the complexation of Ni^{2+} and Co^{2+} by PADA in the presence of different concentrations of NaCl (up to 2.5 M). The increment in the rate constant for complex formation in the presence of an added salt is similar for both metal ions; for example, there is an approximate doubling of the rate constant in the presence of 2.0 M sodium chloride compared with the complex formation of Ni^{2+} and Co^{2+} in aqueous solution. If we take into account the fact that PADA has no charge, on the basis of the treatment by Fuoss,[18] the expectation is that K_{os} will remain nearly constant on changing the ionic strength. For reactions of Ni^{2+} with uncharged ligand, K_{os} has been estimated[19] to be 0.3 $dm^3\,mol^{-1}$. Therefore the dependence of k_1^i on the microemulsion's water content should be related to changes in k_{ex}.

The ratio for the reactivity of Co^{2+} and Ni^{2+} shows that no change occurs in the rate-determining step. In an aqueous medium the ratio of the rate constants for the formation of the Co^{2+}-PADA and Ni^{2+}-PADA complexes is 75, in accordance with the ratio of the rate constants for water exchange.[20] In the interface of the AOT/isooctane/water microemulsions this ratio is approximately 50. The higher reactivity of Co^{2+} is consistent with the existence of an Eigen–Wilkins-type mechanism.

In electrolyte solutions ions are solvated by water molecules (hydration) and are no longer a part of the bulk water. These salt–solvent interactions cause a decrease in water activity as the electrolyte concentration is increased. In this sense, the release of coordinated water is expected to be easier in solutions of high salt concentrations. Hence the first-order rate constant for the exchange of a solvent molecule between the first solvation sphere of the metal ion and the bulk solvent, k_{ex}, would be expected to increase and k_b to decrease. In an electrolyte solution with an ion concentration of 4 mol dm^{-3}, on the assumption that each ion is hydrated in its primary sphere by about six water molecules, the molarity of bulk water is reduced to about one half of its value in dilute solution. There are about 10^5 hydrated sodium ions for each Ni^{2+}-PADA ion produced. The release of coordinated water into an electrolyte solution of high salt concentration is favored more than the release into a solution of low salt concentration. This effect is more pronounced in the microemulsions.[21] If the surfactant molecules were completely dissociated the local concentration of SO_3^- and Na^+ ions in the aqueous droplets would vary between 1.1 M for $W = 50$ up to 55.5 M for $W = 1$. The increase in the ionic strength as W decreases is not so noticeable as a great part of the charge of the interface is neutralized. However the increase in the ionic strength must be sufficient to cause an increase in the rate of water exchange from the $(H_2O)_6Ni^{2+}$ ion such that we can explain the increase in the rate constant for the formation of the Ni^{2+}-PADA complex relative to the value observed in an aqueous medium. An increase in the rate constant for water exchange has also been observed in the formation of the monochelate of Ni^{2+} with heptane-3,5-dione in concentrated aqueous sodium perchlorate solution. The observed positive salt effect on the rate of complex formation can be understood to be a result of an increase in the rate of water exchange from the first solvation sphere of the metal into the bulk solvent with increasing salt concentration.

On the basis of the above discussions it is easy to understand that the rate constant for the dissociation of the complex, k_{-1}^{i}, is approximately independent of the value of W. Hence it is important to understand k_{-1}^{i} in terms of the Eigen–Wilkins mechanism: $k_{-1}^{i} = k_b k_{-rc}/k_{rc}$. According to the above discussion it is expected that k_b will decrease with decreasing W because there is an increase in the saline concentration. The ring-closure process must occur in such a way that in the final product the charge on the Ni^{2+} cation will be delocalized in the ring. Therefore we expect k_{rc} to increase with decreasing W given that as W decreases the capacity for solvation of the charge of the system decreases. The net result is the compensation of the effects produced by the changes in the properties of the medium on the different rate constants.

Conclusions

It was possible to interpret the results obtained from the kinetic study of the formation of the Ni^{2+}-PADA and Co^{2+}-PADA complexes by considering the distribution of the reaction's components in the dispersed water droplets, the continuous oil phase, and the amphiphilic film that separates the oil and water phases. The model developed allows us to obtain the true rate constants for reactions in the interface, as well as the distribution constant of PADA between the continuous medium and the interface, K_{oi}^{PADA}, and the equilibrium constant for the formation of the complex, K. The values obtained for K_{oi}^{PADA} and K from the kinetic data are perfectly compatible with those previously obtained from thermodynamic studies.

The values obtained for the rate constants of formation, k_1^{i}, and dissociation, k_{-1}^{i}, of the complex show that k_1^{i} decreases as the water content of the microemulsion increases, whereas k_{-1}^{i} remains practically constant. The values of both k_1^{i} and k_{-1}^{i} are greater than those obtained in an aqueous medium. The ratio of the rate constants for the formation of the Co^{2+}-PADA and Ni^{2+}-PADA complexes are compatible with an Eigen–Wilkins-type mechanism. Hence the rate constants for the formation and decomposition of the complex are given by $k_1^{i} = K_{os}k_{ex}$ and $k_{-1}^{i} = k_b k_{-rc}/k_{rc}$, respectively. The variations in the rate constant for the formation of the complex as the water content decreases are due to the fact that there is an increase in the ionic concentration within the droplet and consequently the rate of water exchange, k_{ex}, from the $(H_2O)_6Ni^{2+}$ ion increases.

Experimental Section

AOT (Aldrich) was dried in a vacuum desiccator for two days and then used without further purification. The other reagents used were supplied at the highest level of purity commercially available by Aldrich and were used without further purification. Microemulsions were prepared by mixing isooctane, water and a 1.00 M AOT/isooctane solution in the appropriate proportions. Stock solutions containing $Ni(NO_3)_2$ and $Co(NO_3)_2$ were prepared in bidistilled water and then diluted.

Kinetic measurements were carried out with an Applied Photophysics stopped-flow spectrophotometer by mixing equal volumes of PADA solution with solutions containing the metal ion. Complex formation was monitored at 550 nm by following the increase in the optical absorbance of the solution due to the formation of the metal-PADA complex. All experiments were carried out at 25 °C with PADA as the reagent in deficit, [PADA] = $(0.8–1) \times 10^{-5}$ M and $[Ni^{2+}] = (0.1–2.5) \times 10^{-3}$ M. For Co^{2+} complexation a kinetic study was carried out with [PADA] = 3.50×10^{-6} M and $[Co^{2+}]$ in the range of $(0.15–3.37) \times 10^{-4}$ M. The kinetic data always fitted the first-order integrated rate equation satisfactorily ($r > 0.999$). We were able to reproduce the rate constants with an error margin of ±5%.

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