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Spectrophotometric study on micelle-mediated shift in kinetic and equilibrium of complex formation between Ni^{2+} and 2-amino-cyclopentene-1-dithiocarboxylic acid

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Abstract

The significant shift in kinetic and equilibrium behavior of complex formation between Ni^{2+} and 2-amino-cyclopentene-1-dithiocarboxylic acid (ACDA) in a solution of ionic surfactant cetyltrimethylammonium bromide (CTAB) was studied spectrophotometrically in 0.1 M NaBr medium at 30°C. A model based on distributions of ligand (ACDA) and complex $[\text{Ni}(\text{ACDA})_2]$ between aqueous and micellar pseudo-phase was applied to account for the shift in the apparent formation constant and observed pseudo-first order rate constant. Partition constants were evaluated by using a technique based on the principal component analysis method. The proposed model, states that the reaction occurs only in the aqueous phase. Apparent formation constants and the observed rate constants decreased with increasing the micelle concentration. Good agreement between experimental and calculated values indicates that, the applied model provides a good description of the micellar effects on complex formation between Ni^{2+} and ACDA. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 2-Amino-cyclopentene-1-dithiocarboxylic acid; Cetyltrimethylammonium bromide; Principal component analysis method

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1. Introduction

It is well established that, in many cases, rates and pathways of all kinds of chemical reactions can be altered by performing the reactions in micellar media instead of pure bulk solvents. Micelles can concentrate the reactants within their small volumes [1,2], stabilize substrates, intermediates or products [3,4] and orient substrates [5,6] so that ionization potentials and oxidation–reduction properties [7], dissociation constants [8,9], physical properties, quantum efficiencies and reactivities [10] are changed. Thus, they can alter the reaction rate, mechanism, equilibrium position and stereochemistry [11]. Micelles change the effective microenvironment around dissolved solutes and hence their physicochemical properties such as equilibrium constant, spectral profile, etc. It has also been noted that, there are structural similarities between globular proteins and spherical micelles, and analogies between micellar catalysis and phase-transfer catalysis [12]. For these reasons, numerous investigators have focused attention on micelles and reactions in micellar media [13].

The solute–micelle interactions and the distribution of solutes between aqueous and micellar pseudo-phase have been studied extensively in order to explain the properties of aqueous micellar systems [14–20]. These media are used in different areas of analytical chemistry, such as the fluorometric methods [21], in separation methods, and in the buffer solutions in capillary zone electrophoresis [22]. Both separation techniques are capable of simultaneous separation of the ionic and non-ionic components of a mixture as the incorporation of solute partitioning into the micellar pseudo-phase provides an additional degree of separation selectivity. The solute–micelle interactions also can enhance possibility of single and multicomponent kinetic determination [23–25]. The enhanced sensitivity of single component kinetic based determination in micellar media arises mainly from the concentration of reactants in the micellar pseudo-phase. However, micelles can alter the apparent rate constant ratio

of two or more species that interact with a common reagent by differing in partitioning properties of components. As a result micellar aggregates might be of use for resolving mixtures of species with insufficiently different apparent rate constants by applying differential reaction-rate methods [26]. Therefore, these features of solute–micelles interactions can help to overcome many of the analytical problems whereas in many areas of analytical chemistry, micellar systems have only been applied in empirical manner. There is, therefore, a need for additional fundamental studies of analytical micellar systems in order to clearly establish the exact origin of many of the beneficial effects that micelles provide.

The avid interest in studying many novel aspects of sulfur-containing metal chelates has engendered large number of publications during recent years [27–30]. Among these the complexes of 2-amino-cyclopentene-1-dithiocarboxylic acid (ACDA) and some of its derivatives have received considerable attention [30–35] both because they can mimic sulfur protein compounds [36] and also because of their antifungal activity [37]. However, the studies undertaken so far are mostly dealing with the synthesis and structural properties of ACDA and its derivatives and little attention has been given to the analytical behavior of these compounds.

This paper describes exploratory results on the complex formation of Ni^{2+} and ACDA in micellar medium. In the presence of cetyltrimethylammonium bromide (CTAB) micelles the equilibrium constant and the rate of the complex formation between Ni^{2+} and ACDA is found to be markedly dependent on the concentration of CTAB. For accurate determination of partition constants of species (ligand and complex), a principal component analysis technique (Kubista's method [38,39]) was used.

2. Experimental

UV-Visible absorbance digitized spectra with

five data points per nanometer were collected using a PHILIPS 8750 spectrophotometer 1-cm quartz cell, a scan rate of 100 nm/min and a slit width of 2 nm. In all measurements the temperature was maintained constant at $30 \pm 0.2^\circ\text{C}$ using a Lo-Templol 154 precision scientific thermostat. Measurements of pH were made with a Metrohm 691 pH-meter using a combined glass electrode. The absorbance measurements as a function of time, at fixed wavelengths, were made with a PHILLIPS PU875 spectrophotometer attached to a Pentium 200 MHz computer. Singular value decomposition (SVD) was performed using MATLAB for windows. All curve fittings were performed either by the Excell solver 97 [40] or Kinfit Program [41].

ACDA was prepared according to the procedure described by Takeshima et al. [42]. Fresh 10^{-3} M solutions were prepared daily by dissolving the reagent in triply distilled water. CTAB (Merck) was used without further purification. Reagent grade nitrate salt of nickel $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, Merck] was used without further purification. Specific details are given in Section 3.

2.1. Procedure for the determination of the formation constant of Ni-ACDA complex in the micellar volume

In order to determine the apparent stability constant of the $\text{Ni}(\text{ACDA})_2$ complex a series of solutions (10 ml total volume) containing a fixed concentration of CTAB above its cmc (0.01–0.08 M), NaBr (0.1 M), ACDA (1.2×10^{-4} M) and various concentration of Ni^{2+} at pH 3 (0.002 M sodium citrate buffer) were prepared. An aliquot of each solution was transferred into a 1-cm quartz cell, thermostated at 30°C and the absorbance was measured at 538 nm. The obtained mole ratio plots clearly showed 1:2 (metal/ligand) stoichiometry. For evaluation of the apparent stability constant in each CTAB micelle concentration from the absorbance vs. total metal ion concentration, a non-linear least squares curve fitting program, Kinfit, was used [41].

2.2. Procedure for the determination of the rate constants of Ni-ACDA complexation reaction in the micellar medium

Kinetic data from the Ni-ACDA reaction was obtained by monitoring the absorbance vs. time at a wavelength of maximum absorbance of the complex under pseudo-first order conditions. In order to evaluate the observed first-order rate constant, k_{obs} , a series of solutions (10 ml total volume) containing a fixed excess concentration of ACDA (8.5×10^{-4} M, approx. 50 times the Ni^{2+} concentration), NaBr (0.1 M) and various concentrations of CTAB above its cmc (0.02–0.15 M) at pH 3 (0.002 M sodium citrate buffer) was prepared. An aliquot (2 ml) of each solution was transferred into a 1-cm quartz cell and thermostated at 30°C . Monitoring of absorbance vs. time was started just after the injection of $10 \mu\text{l}$ Ni^{2+} solution to create $1 \mu\text{g}/\text{ml}$ concentration of Ni^{2+} in the cell. For evaluation of the observed rate constant at each CTAB micelle concentration, the exponentially increasing absorbance-time data was fitted by the Excel solver program [40].

3. Results and discussion

Shift in absorption spectra, acid-base equilibria and complex formation constants due to interactions of solutes with micelles have been shown frequently [15,16,43,43]. Several models have been proposed to discuss these changes in chemical and physical properties. Binding equilibria [24,44,45] between solute and micelle aggregates, the partition equilibria [39,44,46] of solutes between aqueous and micellar pseudo-phase and the ion-exchange equilibria [47,48] are the most applicable models. The partition model is one of the most successful models in which it is assumed that micelles acts as a separate phase uniformly distributed through the solution, and distribution of neutral species and ion associates between the aqueous phase and micelle can occur. However, it was shown that the partition model, regardless of

specific solute–micelle interaction can be used in solution of ionic surfactants, provided that the surfactant concentration is sufficiently above its critical micelle concentration and that the concentration of the background electrolyte is much higher than those of the solutes [16]. Under these experimental conditions, the partition model provides tools for the study of the micelle–solute interactions; first of all, the partition model can be applied to ionic and non-ionic surfactants, regardless of the specific solute–micelle interactions. So the comparison of the equilibrium and rate constants for a given system in different surfactant solutions yield a direct comparison in terms of the extent of solute–micelle interaction for the different species or the ability of solubilization of surfactants studied.

ACDA is a monoprotic acid that can exist in solution as its neutral, acidic or anionic basic form [49]. Spectral changes of ACDA solution as a function of pH in a 0.1 M concentration of NaBr electrolyte (Fig. 1) was used for determination of the dissociation constant of the acid. A simple and accurate full spectrum method was used for this purpose [50] and the p function of the calculated acidity constant (pK_a) was found to be 5.42 ± 0.02 . Therefore, at pH 3 which was selected for further studies ACDA exists in its neutral form.

The distribution of each species (ligand or complex) between the two phases is defined by the chemical equilibrium:



The corresponding partition constant, K_p , is,

$$K_p = \frac{[S]_m}{[S]_w} \quad (2)$$

The subscript m or w indicates the concentration of the species in micellar and aqueous phases, respectively. The absorbance of each species, ligand or complex, at any wavelength in the presence of both phases is denoted as A_t which is equal to:

$$A_t = \varepsilon_w \frac{(1-R)C_t}{1-R+K_p R} + \varepsilon_m \frac{K_p RC_t}{1-R+K_p R} \quad (3)$$

ε_w and ε_m are the species molar absorptivities as a function of wavelength in aqueous and micellar phases, respectively, C_t is total concentration of species in both phases and R is the ratio of the micellar volume to the total volume of solution which can be written as,

$$R = \frac{V_m}{V} = (C_{CTAB} - cmc)V_\phi \quad (4)$$

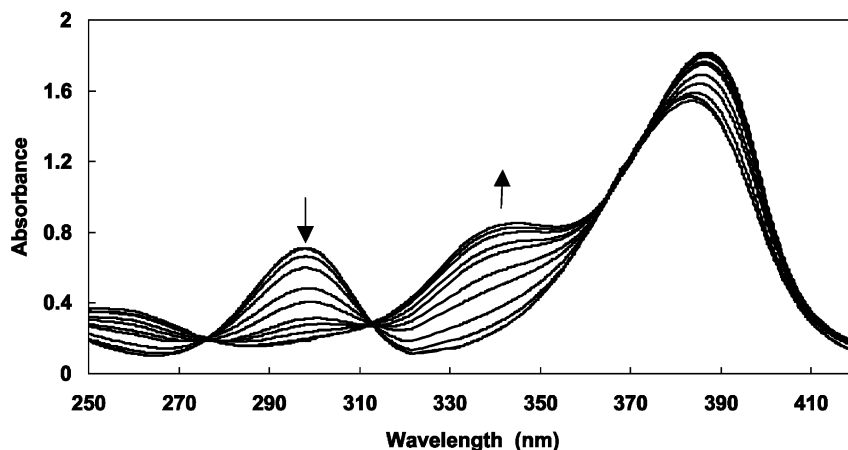


Fig. 1. Absorption spectra of ACDA (4.2×10^{-5} M) in aqueous solution as a function of pH. pH 3.8, 4.4, 4.9, 5.4, 5.5, 5.8, 6.0, 6.3, 6.6, 6.9.

where C_{CTAB} is the total concentration of CTAB surfactant, cmc is the critical micelle concentration (both in mol l^{-1}) and V_{ϕ} is the partial molar volume of micellized surfactant (l mol^{-1}).

For the treatment of the distribution equilibria in micellar phase, a technique that is based on principal component analysis (PCA) of a spectral matrix followed by transformation of the abstract vectors into real spectra and concentrations, was used [39]. In summary, the applied approach for the deconvolution of micellar spectra includes the following steps: (i) defining the system in terms of parameters that are known and those which are ultimately required to be calculated (e.g. Eqs. (1)–(4)); (ii) performing the singular value decomposition (SVD) on a matrix comprised of spectra recorded at different but known surfactant con-

centrations (Fig. 2) to obtain two matrices, one corresponding to abstract spectra and the other to the abstract concentration; (iii) introducing a transformation matrix to transform the abstract matrices into real matrices corresponding to molar absorptivities and concentrations; (iv) finding the elements of the transformation matrix by globally regression [38] of the abstract vectors against known system parameters; and (v) using the transformation matrix to calculate the real species spectrum and concentration in the micellar phase free from contributions in aqueous phase.

Fig. 2 shows typical absorption spectra of ACDA and Ni-ACDA complex (at pH = 3 and 0.1 M NaBr) as a function of CTAB concentration sufficiently beyond its cmc. Apparent changes in absorption spectra of each species, is due to

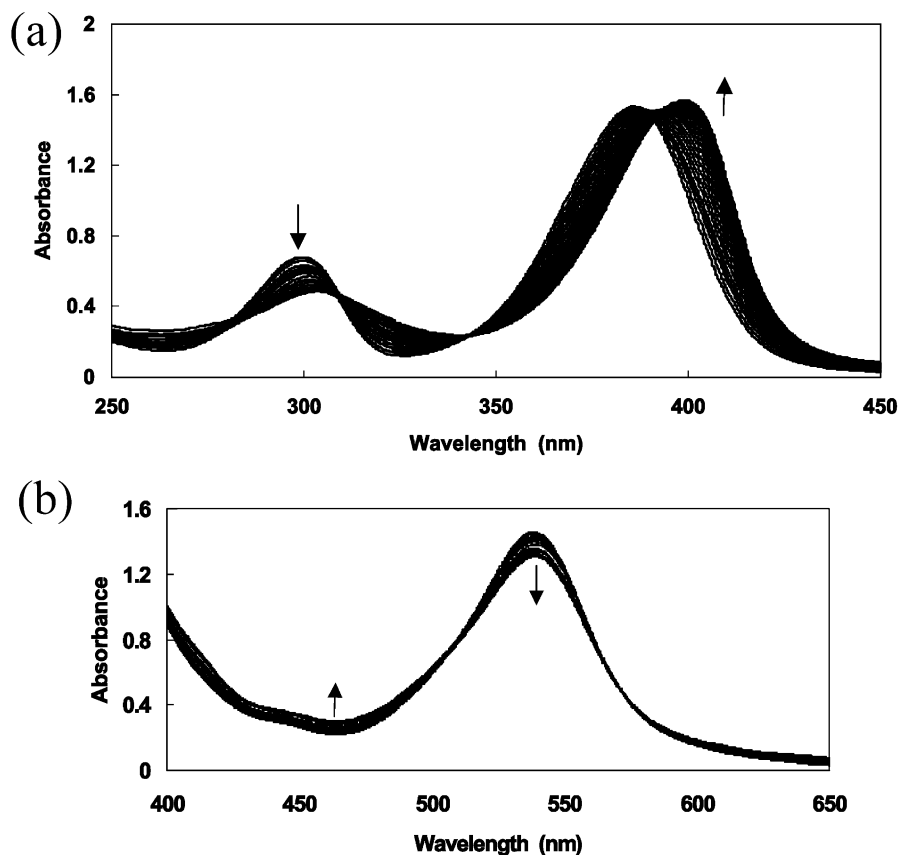


Fig. 2. Apparent absorption spectra of: (a) ACDA; and (b) Ni(ACDA)₂ as a function of CTAB concentration. Arrows indicate the spectral trends in changing C_{CTAB} from 0.001 to 0.01 M for Fig. 2a and from 0.013 to 0.059 M for Fig. 2b.

the distribution process of ligand or complex, by increasing the volume of the micellar phase (i.e. with increase in total CTAB concentration). This incorporation of each species in the CTAB micelle can be regarded both as microenvironmental effects of the micelle and solubilization effects. Decomposition of spectral set data by SVD and performing further analysis lead to accurate evaluation of partition constants of the ACDA and Ni-ACDA complex. Under working conditions (large excess of background electrolyte with respect to the solute, $C_{\text{NaBr}} = 0.1$ M, C_{ACDA} or $C_{\text{Ni(ACDA)}_2}$ approx. 1×10^{-4} M and low concentration of buffer, approx. 0.002 M), the cmc of CTAB is 7.0×10^{-5} M and $V_\phi = 0.361$ l mol⁻¹ [16] and distribution constant for ACDA and Ni(ACDA)₂ were obtained as 742.75 and 4.75, respectively. These important parameters (K_p values of ligand and complex) accompanied with an appropriate model can be used for predicting the influence of micelle concentration on apparent equilibrium and kinetic behaviors of complex formation between nickel and ACDA.

The apparent formation constants of the Ni-ACDA complex at different CTAB concentrations were obtained at 30°C, pH 3 and 0.1 M concentration of NaBr, by curve fitting of absorbance–mole ratio data to a 1:2 (metal/ligand) stoichiometric model. All apparent formation constant values evaluated from the computer fitting of the corresponding absorbance–mole ratio data are listed in Table 1. Because of the low solubility of the Ni complex of ACDA, evaluation of the formation constant in the absence of the micelle, CTAB was not possible. The apparent formation constant (K_f^*) for the Ni(ACDA)₂ complex is defined as:

$$K_f^* = \frac{[\text{Ni(ACDA)}_2]^*}{[\text{Ni}^{2+}][\text{ACDA}]_*^2} \quad (5)$$

where $[\text{Ni(ACDA)}_2]^*$ and $[\text{ACDA}]_*$ are the total concentration of the complex and ligand, regardless of whether they are in aqueous or micellar phase. Because of the large excess of the background electrolyte with respect to the Ni²⁺ ion, the interaction of Ni²⁺ with the micellar phase is

Table 1

Apparent observed rate constants and equilibrium constants of complex formation between Ni²⁺ and ACDA at different ratios of micellar volume to the total volume in 0.1 M NaBr and 30°C

k_{obs}	R	K_f^*	R
0.256 ± 0.001	0.0094	$(3.78 \pm 0.05) \times 10^{12}$ ^a	0
0.207 ± 0.002	0.0132	$(1.76 \pm 0.10) \times 10^{11}$	0.0049
0.135 ± 0.001	0.0189	$(1.03 \pm 0.10) \times 10^{11}$	0.0074
0.091 ± 0.003	0.0283	$(5.20 \pm 0.15) \times 10^{10}$	0.0099
0.094 ± 0.002	0.0340	$(3.78 \pm 0.12) \times 10^{10}$	0.0123
0.086 ± 0.001	0.0378	$(3.33 \pm 0.20) \times 10^{10}$	0.0148
0.077 ± 0.002	0.0416	$(1.90 \pm 0.10) \times 10^{10}$	0.0173
0.077 ± 0.001	0.0473	$(1.79 \pm 0.11) \times 10^{10}$	0.0197
0.066 ± 0.002	0.0492	$(1.28 \pm 0.10) \times 10^{10}$	0.0247
0.066 ± 0.002	0.0567	$(5.62 \pm 0.23) \times 10^9$	0.0296

^aObtained from fitting of Eq. 5.

supposed to be negligible and thus its distribution between the two phases are not considered in the model. According to this model the relation between apparent formation constant, K_f^* , and the ratio of micellar volume to the total volume, R , is defined as:

$$K_f^* = K_f \left(\frac{1 + K_{p(\text{complex})}R}{(1 + K_{p(\text{ligand})}R)^2} \right) \quad (6)$$

where $K_{p(\text{complex})}$ and $K_{p(\text{ligand})}$ are the partition constants of the complex and the ligand, respectively and K_f is the formation constant of the Ni(ACDA)₂ complex in aqueous media. A plot of apparent formation constants as a function of R is shown in Fig. 3. The good agreement between experimental and calculated values of K_f^* (according to Eq. (6)) shows that this proposed model provides a complete description of the influences of CTAB concentration on the apparent formation constant of the complex. From this curve fitting the conditional complex formation constant in aqueous media can also be obtained (Table 1). Thus, the ability of micelles to solubilize the Ni-ACDA complex can be one of the main reasons for the change in complex formation constants in different concentrations of CTAB (cf. Fig. 2b and Table 1). In fact the requirement for intact micelles supports a strong dependence upon micelle solubilization rather than direct surfac-

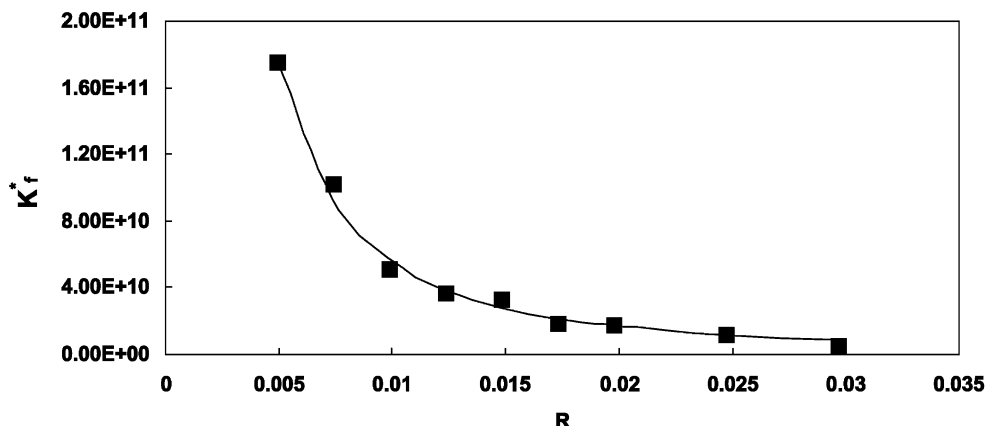
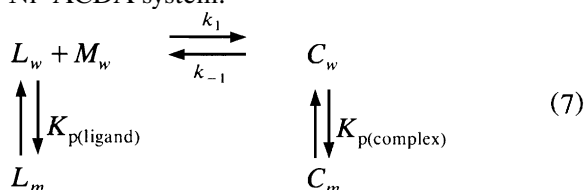


Fig. 3. Apparent complex formation constants of Ni(ACDA)₂ in micellar media as a function of volume ratio, *R*. The least-squares fit according to Eq. (6) is shown as a solid line.

tant–ligand interactions as the source of these effects.

The micellar effects upon complex-formation kinetics have also been studied. On the basis of the above information, the following model is employed in the analysis of kinetic data for the Ni–ACDA system:



In this model, the chemical reaction is assumed to occur only in aqueous phase and distribution of the metal ion (*M*) between the two phases, is supposed to be negligible (due to the relatively high concentration of background electrolyte).

Under pseudo-first-order conditions ($[L]_0^* \gg [M]_0$) the observed first-order rate constant is given by:

$$k_{\text{obs}} = \frac{k_1 [L]_0^*}{(1 + K_{p(\text{ligand})} R)(1 + K_{p(\text{complex})} R)} + \frac{k_{-1}}{1 + K_{p(\text{complex})} R} \quad (8)$$

It is also assumed, as the previous studies [24,51] that, partitioning of the reacting species between

the pseudo-phases is rapid compared to the rate of chemical reaction.

In order to investigate the kinetics of complex formation, the absorbance of 538 nm [wavelength of maximum absorption band of Ni(ACDA)₂] was monitored as a function of time under pseudo-first-order conditions at 30°C and different concentrations of CTAB. The observed rate constants were then evaluated from fitting the absorbance–time data to the following simple exponential equation:

$$A_t = A_\infty (1 - e^{-k_{\text{obs}} t}) \quad (9)$$

where A_∞ and A_t are the absorbances at infinite and any time, respectively. A plot of observed pseudo-first order rate constants as a function of *R* is shown in Fig. 4. As expected, because of the reaction occurring only in the aqueous phase (according to the model) and different tendency of reactant and product to the micellar pseudo phase, with increasing the micelle concentration the observed rate constants are decreased. The kinetic parameters, k_1 and k_{-1} were also obtained from fitting the data shown in Fig. 4 to Eq. (8) ($k_1 = 2526.1$ and $k_{-1} = 5.78 \times 10^{-3}$). The good agreement between experimental and calculated pseudo-first order rate constants shows that the proposed model provides a complete description of the effects of the CTAB micelle on the kinetics

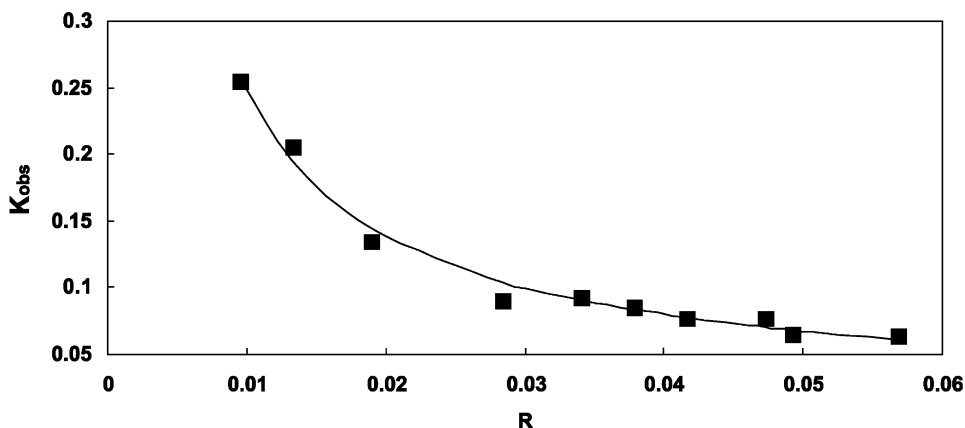


Fig. 4. Apparent observed rate constant in micellar media as a function of volume ratio, R . The least-squares fit according to Eq. (8) is shown as a solid line.

of complex formation. As mentioned previously, in the proposed model it is assumed that the chemical reaction taking place in the bulk solution and the reaction associated with the micelle aggregates is supposed to be negligible due to low partitioning of Ni^{2+} in the micelle. It has also been assumed that partitioning the reactant and product between two pseudo-phases was quite fast compared to the rate of chemical reaction.

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