Micellar Effect on the Formation Rate of Ni(II) and Co(II) Complexes with 8-Quinolinol and Its 5-Alkyloxymethyl-8-quinolinol Derivatives in a Nonionic Surfactant Micellar System

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(Received June 26, 1991)

Synopsis. In the Triton X-100 micellar system, ligands such as 8-quinolinol and 5-alkyloxymethyl-8-quinolinol were distributed between the aqueous and micellar phases. The Ni(II) and Co(II) complexes were formed in both phases and their reaction rate constants in the aqueous phase were 2.8×10^3 and 1.3×10^5 mol^{-1} dm^3 s^{-1}, respectively. The reaction rates in the micellar phase were about one-tenth those in the aqueous phase. The distribution of ligand into the micellar phase delayed the observed reaction rate.

The solubilizing power and catalytic property exhibited by the surfactant micelle are very useful in the field of analytical chemistry.[1] Many applications have been found in spectrophotometric analysis of metal ions to dissolve sample and reagent, to improve sensitivity, to control reaction rates, and to induce a favorable shift in equilibrium constants. Most of the observed effects were rationalized in terms of the distribution of reactants between the aqueous and micellar phases. For the ionic micellar system, deviations from the distribution equilibrium model can be corrected by taking into account the ion-exchange processes at the charged micellar surface.[1,2]

The nonionic surfactant micelle lacks the electrostatic interactions on the micellar surface. The distribution equilibrium models based on the classical Hartley micelle have been used to explain the shift of equilibrium constants[3] such as acid dissociation constants of ligands and formation constants of metal complexes. However, there are a few studies concerning the exact kinetic and mechanistic step involved in the formation of the metal complex. Ito and co-workers[4] reported that the observed reaction rates of Ni(II) with 8-quinolinol decreased with increasing surfactant concentrations above the cmc (critical micellar concentration). This was explained by the postulations that the dissolved ligand in the micelle could not react with metal ions and the reactions occurred only in the aqueous phase. In the present study, taking into account the reactions in the micellar phase, the formation rate of Ni(II) and Co(II) complexes with 8-quinolinol and its derivatives was investigated in nonionic surfactant (Triton X-100) solutions.

Experimental

Reagents. Water that had been deionized and distilled was used in the preparation of all solutions. 8-Quinolinol (Kanto, QN) was twice purified with ethanol. Seven derivatives (RQN) of 5-alkyloxymethyl-8-quinolinol (alkyl=methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, and heptyl- [abbreviated MEQN, ETQN, PRQN, BUQN, PEQN, HEQN, and HPQN, respectively]) were synthesized according to the methods in the literature and purified twice with hexane.[5] The nonionic surfactant, Triton X-100 (Katayama), was dissolved in water and a molar concentration was calculated assuming an average molecular weight of 625. Approximately 0.01 mol dm^{-3} acidic solutions of Ni(II) sulfate and Co(II) nitrate were prepared and standardized by titration with EDTA. All other chemicals used were of analytical grade purity. Sodium perchlorate was used to adjust the ionic strength to 0.05. A final concentration of 5.0×10^{-3} mol dm^{-3} phosphate buffer was used to maintain a constant pH of 7.0.

Apparatus. The kinetic measurements were carried out with a Union Giken stopped-flow spectrophotometer, model RA-701, having an observation cell with a 0.20 cm light path. This apparatus was kept at a constant temperature of 25±0.1 °C. The solubility of QN and RQN in water or surfactant solutions was obtained by an absorption measurement with a Shimadzu UV-265 double beam spectrophotometer. A Horiba M-7 pH meter was used for all pH measurements.

Procedure. Measurement of Solubility. Solubilities of QN and RQN were spectrophotometrically determined in water and Triton X-100 solutions containing the phosphate buffer and sodium perchlorate. The solution which contained an excess of QN or RQN was shaken for three days and any undissolved portion was filtered off. After dilution to the proper concentration with water, hydrochloric acid was added to about pH 1. The absorbance of the solutions was measured at 360 nm against a water blank.

Measurement of Reaction Rate. A pair of solutions were prepared for the kinetic studies as a function of Triton X-100 concentrations. One contained the buffer, sodium perchlorate and 5.0×10^{-4} mol dm^{-3} QN or RQN while the other contained 1.0×10^{-5} mol dm^{-3} Ni(II) or Co(II). Triton X-100 was added to both solutions. The solutions were injected into the optical cell through the mixer of the stopped-flow spectrophotometer. The change in absorbance was measured at 380 nm versus time. The pH of the solutions was measured just after the kinetic runs.

Results and Discussion

Distribution Constant. In the measurements at pH 7.0, most ligands existed as a neutral form and the anionic form was neglected (less than 0.5%). The distribution constant of the ligands, K_{dm}, was defined as

$$K_{\mathrm{dm}} = [\mathrm{HL}]_{\mathrm{m}}/[\mathrm{HL}]_{\mathrm{a}}, \tag{1}$$

where the subscripts m and a denote the micellar and aqueous phases, respectively. The concentration of ligands in the micellar phase ($[\mathrm{HL}]_{\mathrm{m}}$) was calculated by subtracting the solubility in water (S_{w}) from that in a surfactant solution (S).

$$[\mathrm{HL}]_{\mathrm{m}} = (S-S_{\mathrm{w}})/V_{\mathrm{m}}, \tag{2}$$

$$[\mathrm{HL}]_{\mathrm{a}} = S_{\mathrm{w}}/V_{\mathrm{a}}. \tag{3}$$

The volume fractions of the micellar phase, V_m, and the aqueous phase, V_a, were calculated by the previously reported method.[6] Equation 4 is obtained from Eqs. 1—3

$$S/S_w = K_{dm}(V_m/V_a) + 1. \tag{4}$$

The solubility (S or S_w) was obtained from the absorbance measurement at Triton X-100 concentrations 0, 0.1, 0.5, 1.0 and 2.0 wt%. The distribution constant (K_{dm}) was obtained from a slope of plot according to Eq. 4 and is summarized in Table 1.

Kinetics. Experiments were performed under the conditions of a pseudo-first-order reaction in the presence of a large excess of ligands. The observed reactions were first-order with respect to the metal ions.

$$-d[M]/dt = k_{obsd}[M], \tag{5}$$

where k_{obsd} is an observed reaction rate constant. Figure 1 shows the effect of Triton X-100 concentration on the reactions. The observed reaction rate constant (k_{obsd}) decreased with increasing surfactant concentrations for all ligands, but this tendency was reduced by increasing the size of the ligands.

In the surfactant solutions, the reaction rates were related to the concentration of the ligands in the aqueous and micellar phases and the phase volumes.

$$k_{obsd} = k_a[HL]_a V_a + k_m[HL]_m V_m. \tag{6}$$

In this equation,[7] k_m and k_a denote the reaction rate constants in the micellar and aqueous phases, respectively. When the value of V_m is negligibly small and V_a is regarded as unity, Eq. 6 can be rewritten using K_{dm} as

$$k_{obsd}/[HL]_a = k_a + k_m K_{dm} V_m. \tag{7}$$

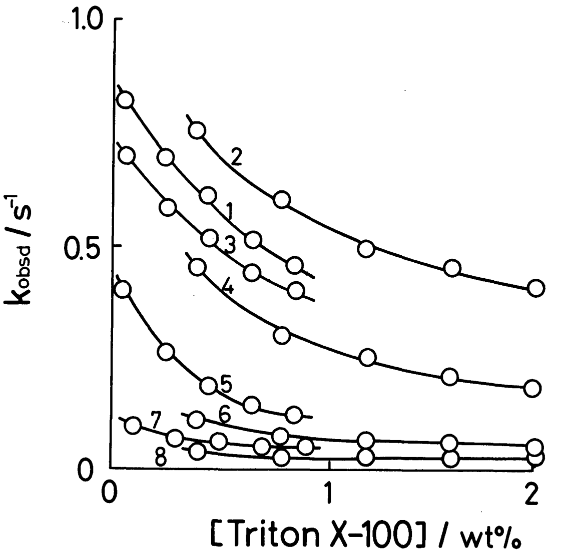

Fig. 1. Dependence of the observed reaction rates for Ni(II)-RQN complexes on Triton X-100 concentrations: [Ni(II)], 5.0×10^{-6} mol dm^{-3}; [RQN], 2.5×10^{-4} mol dm^{-3}. 1, QN; 2, MEQN; 3, ETQN; 4, PRQN; 5, BUQN; 6, PEQN; 7, HEQN; 8, HPQN.

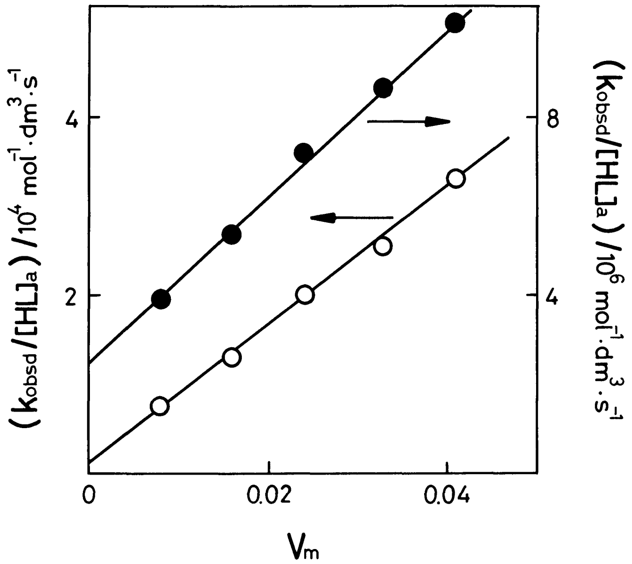

Fig. 2. Plots of $k_{obsd}/[HL]_a$ vs. V_m for Ni(II)-HPQN and Co(II)-HPQN complexes: [Metal], 5.0×10^{-6} mol dm^{-3}; [HPQN], 2.5×10^{-4} mol dm^{-3}; ○, Ni(II)-HPQN; ●, Co(II)-HPQN.

Table 1. Distribution Constants of QN and RQN and Formation Rate Constants of the Ni(II) and Co(II) Complexes in Micellar and Aqueous Phases

	QN, RQN	Ni(II) complex		Co(II) complex	
	log K_{dm}	$k_m/10^2$ dm^3 mol^{-1} s^{-1}	$k_a/10^3$ dm^3 mol^{-1} s^{-1}	$k_m/10^4$ dm^3 mol^{-1} s^{-1}	$k_a/10^5$ dm^3 mol^{-1} s^{-1}
QN	1.80, 1.66[a]	3.5	3.5	1.2	1.3
MEQN	1.67	3.9	3.9	2.5	1.3
ETQN	1.76	2.9	2.9	0.79	1.1
PRQN	2.11	3.0	3.2	0.95	1.3
BUQN	2.69	1.7	3.1	0.59	1.2
PEQN	3.03	1.1	2.3	0.66	1.2
HEQN	3.59	1.9	2.5	0.51	0.89
HPQN	3.79	1.2	1.2	0.32	2.5
Average		2.4±0.9	2.8±0.7	0.94±0.58	1.3±0.4

a) By 1-butanol-water extraction method.[13]

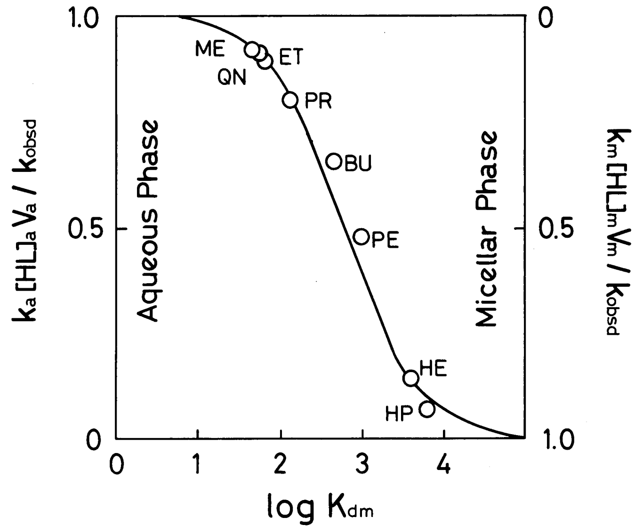

Fig. 3. Plot of contribution of the complex formation in the aqueous phase or in the micellar phase vs. the logarithm of the distribution constant of RQN for the formation of the Ni(II)-RQN complex at 1.0wt% Triton X-100 concentration.

Figure 2 shows the plot of $k_{\mathrm{obsd}}/[\mathrm{HL}]_{\mathrm{a}}$ vs. V_{m} according to Eq. 7 for Ni(II) and Co(II) complexes with HEQN. An intercept gave the reaction rate constant (k_{a}). The reaction rate constant (k_{m}) was obtained from the slope divided by K_{dm}. The results are summarized in Table 1. The rates 3.6×10^3 mol^{-1} dm^3 s^{-1} obtained by the chloroform extraction method$^{8)}$ and 1.3×10^3 mol^{-1} dm^3 s^{-1} by the stopped-flow method$^{9)}$ were reported as the reaction rate constant for the Ni(II)-QN complex in water. Although the values of k_{a} for Ni(II)-RQN complexes in Table 1 showed some scatter, these values were close to the rate constant in water and were constant. The k_{a} value in the micellar system has been considered to be the same as that in water, on the other hand, the reaction rate in the micellar phase (k_{m}) may be affected by the nature of the reactants and the location or orientation in the micelle.$^{10)}$ The large and hydrophobic ligands are deeply sunk in the internal portion of the micelle, therefore they have smaller reaction rate constants.

From the calculation of the right hand first term and/or second term in Eq. 6, we elucidated the degree of the complex formation in the phases. Figure 3 shows a contribution of reactions of each phase to the formation of the Ni(II)-RQN complexes at 1.0 wt% Triton X-100. The difference between the values of k_{m} in Table 1 is not large, so the solid line was calculated from the average values. In the case of ligands such as HEQN and HPQN having a large distribution constant, the complex formation preferentially occurred in the micellar phase. On the contrary, complexes with small ligands such as QN and MEQN were formed in the aqueous phase. A boundary condition was the distribution constant of about 1000. The same results were obtained for the Co(II)-RQN complexes.

Not only the acceleration, but also inhibition caused by the micelle will be important in the kinetic analysis of metal ions. Because many formation reactions of metal complexes with common ligands are so rapid, computers and various instruments such as stopped-flow spectrophotometers have been used to analyze mixtures of more than two metal ions.$^{11)}$ For the application of conventional methods with primitive spectrophotometers or FIA kinetic methods, the slower reaction is available, i.e. more than 10 s$^{12)}$ may be required. The nonionic micellar system can modify the reaction rates between k_{a} and k_{m} owing to the hydrophobicity of the ligands.

This work was supported by a Grant-in-Aid for Scientific Research No. 2640450 from the Ministry of Education, Science and Culture. We acknowledge Professor H. Freiser of The University of Arizona for his helpful discussions.

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7) The equation is identical with the general equation which was described by using a binding constant. For example, the binding constant (K_{bind}) is defined as $K_{\mathrm{bind}}=L_{\mathrm{m}}/(L_{\mathrm{a}}D_{\mathrm{m}})$, where L_{m} and L_{a} are the concentration of reactants binding and unbinding to the micelle, respectively, and D_{m} is the surfactant concentration forming the micelle. $k_{\mathrm{obsd}}=(k_{\mathrm{a}}+k_{\mathrm{m}}K_{\mathrm{bind}}D_{\mathrm{m}})L_{\mathrm{a}}$ in L. S. Romsted, "Surfactants in Solution," ed by K. L. Mittal and B. Linden, Plenum Press, New York (1984), Vol. 2, p. 1025. There are following relations: $L_{\mathrm{a}}=[\mathrm{HL}]_{\mathrm{a}}V_{\mathrm{a}}/(V_{\mathrm{a}}+V_{\mathrm{m}})$, $L_{\mathrm{m}}=[\mathrm{HL}]_{\mathrm{m}}V_{\mathrm{m}}/(V_{\mathrm{a}}+V_{\mathrm{m}})$ and $V_{\mathrm{a}}+V_{\mathrm{m}}=1$, respectively.

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