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Ion-pair Extraction of Nickel(II) and Copper(II) Complexes of 8-Hydroxy-7-nitroso-5-quinolinesulfonic Acid with Zephiramine

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The ion-pair extraction of nickel(II) and copper(II) complexes of 8-hydroxy-7-nitroso-5-quinolinesulfonic acid (H_2NQS) with zephiramine(benzyldimethyltetradecylammonium chloride) was studied. It was found that slope analysis can be used to determine the mechanism of these ion-pair extraction systems, as well as the continuous-variation method for three component systems or the mole-ratio method by choosing appropriate extraction conditions. As a result, the equation of these extraction equilibria can be represented as:

$$M^{2+} + 2HNQS^- + 2ZCl_{(o)} \rightleftharpoons M(NQS)_2Z_{2(o)} + 2H^+ + 2Cl^-$$

The extraction constants and the exchange constants were calculated.

As has previously been stated,[1] the author has applied 8-hydroxy-7-nitroso-5-quinolinesulfonic acid (H_2NQS) as a chelating reagent to the solvent extraction of the ternary complex, which is an ion-pair of water-soluble metal chelate with zephiramine (benzyldimethyltetradecylammonium chloride), in order to develop a sensitive colorimetric method for determining cobalt(II) and iron(II).

Since this reagent forms stable complexes with many other bivalent metal ions, in the present study it was applied to the solvent extraction of nickel(II) and copper(II). Subsequently, the compositions of extracted species were investigated. As a rule, the mechanism of ion-pair extraction is very complicated, as it includes a greater number of related chemical species than that of chelate extraction. For example, Kambara *et al.*[2,3] have presented a continuous-variation method for three components or a mole-ratio method to analyze the compositions of extracted species in the ion-pair extraction system. The compositions of ternary complexes of metal(Ni(II) and Cu(II)), 8-hydroxy-5-quinolinesulfonic acid (H_2QS) and zephiramine (ZCl) were reported by them to be $Ni(QS)_2(HQS)Z_3$(λ_{max}=400 nm, $\varepsilon = 1.35\times10^4$) and $Cu(QSZ)_3$ (λ_{max}=410 nm, $\varepsilon = 9.45\times10^3$).

The present author has been attempted to apply a simple slope analysis, which is usually used in a chelate extraction system, to determine the compositions of extracted species in this extraction system. As a result, it could be seen that the slope analysis as well as the mole-ratio method can be successfully used for the ion-pair extraction system by choosing appropriate extraction conditions. The composition of the extracted species in this extraction system was confirmed to be 1:2:2 (M:H_2NQS:Z) for both the ternary complexes of nickel(II) and copper(II), differrent from the 1:1 complex synthesized in the auqeous phase by Aly *et al.*[4] In addition, the extraction constant of the complexes and the exchange constant between NQS and Cl^- were calculated from the distribution ratios in order to understand the extraction equilibria quantitatively.

Experimental

Reagents. Stock solutions of nickel(II) and Copper (II) (1000 ppm each) were prepared by dissolving weighed amounts of nickel sulfate and copper sulfate in water distilled and subsequentry standardized atomic absorptionmetrically, and diluted with distilled water as required.

The buffer solutions used were mixtures of a 0.2 M (1 M= 1 mol dm^{-3}) solution of sodium acetate and acetic acid for measurement at pH 3.9, and that of a 0.2 M solution of sodium borate and boric acid for measurement at pH 8.9. The ionic strength of the aqueous solutions used was kept at 0.1 with sodium sulfate and a small amount of buffer solutions, such as acetate and borate buffers. For low pH ranges, the ionic strength of the aqueous solutions was kept at 0.1 with mixtures of sodium sulfate, sulfuric acid, and sodium acetate.

All the other chemicals and apparatus used were essentially the same as those described earlier.[1]

Extraction Procedure. Ten ml of a buffered solution containing an appropriate amount of H_2NQS and nickel(II) or copper(II) was shaken with an equal volume of a chloroform solution of zephiramine. The pH value of the aqueous phase after extraction was taken as the equilibrium pH value. After a 3-min centrifugation(2000 min^{-1}), the phases were separated. The aqueous phase was immediately analyzed by atomic-absorption spectrophotometry, while the organic phase was analyzed after back-extraction into dilute hydrochloric acid.

Results and Discussion

Optimum Conditions for Extraction. The effect of the pH and the shaking time on the extraction percentage of Ni(II)–NQS and Cu(II)–NQS complexes with zephiramine were examined. Figure 1 shows that nickel and copper were quantitatively extracted in the pH ranges of 4.0—11.0 and 3.5—5.5 respectively.

A shaking time of 5 min was sufficient to establish equilibrium in all the systems.

Extraction Exchange Constant of H_2NQS Species. Since the values of the acid dissociation constants of H_2NQS are given as $pK_{a_1} < 1$ and $pK_{a_2} = 5.55$,[1] the dianion NQS^{2-} is the predominant H_2NQS species above pH 6.5, and the monoanion $HNQS^-$, below pH 4.5. These species are also extracted into the organic phase with zephiramine.

The equations of the extraction equilibria of H_2NQS with zephiramine can be represented as follows for both the cases:

at pH 3.9

$$HNQS^- + ZCl_{(o)} \rightleftharpoons HNQSZ_{(o)} + Cl^-, \qquad (1)$$

at pH 8.9

$$NQS^{2-} + 2ZCl_{(o)} \rightleftharpoons NQSZ_{2(o)} + 2Cl^-. \qquad (2)$$

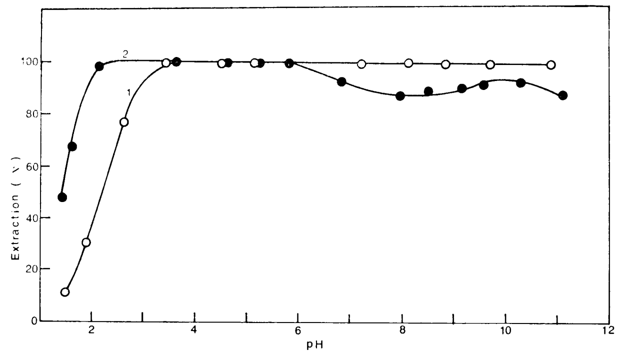

Fig. 1. The dependence of percentage extraction of nickel(II) and copper(II) complexes on the pH of the aqueous phase.
$[\mathrm{NQS}]=3.16\times10^{-4}$ M, $[\mathrm{ZCl}]=10^{-3}$ M. 1: $[\mathrm{Ni}]=3.40\times10^{-5}$ M, 2: $[\mathrm{Cu}]=3.15\times10^{-5}$ M.

The extraction exchange constants of H_2NQS and Cl^- are given by:

$$K^{\mathrm{Cl^-}}_{\mathrm{HNQS^-}}=\frac{[\mathrm{HNQSZ}]_o[\mathrm{Cl^-}]}{[\mathrm{HNQS^-}][\mathrm{ZCl}]_o}, \tag{3}$$

$$K^{\mathrm{Cl^-}}_{\mathrm{NQS^{2-}}}=\frac{[\mathrm{NQSZ_2}]_o[\mathrm{Cl^-}]^2}{[\mathrm{NQS^{2-}}][\mathrm{ZCl}]_o^2}. \tag{4}$$

By taking logarithms of Eqs. 3 and 4, the following expression is derived:

$$\log\frac{[\mathrm{HNQSZ}]_o}{[\mathrm{HNQS^-}]}=\log K^{\mathrm{Cl^-}}_{\mathrm{HNQS^-}}-\log\frac{[\mathrm{Cl^-}]}{[\mathrm{ZCl}]_o}, \tag{5}$$

$$\log\frac{[\mathrm{NQSZ_2}]_o}{[\mathrm{NQS^{2-}}]}=\log K^{\mathrm{Cl^-}}_{\mathrm{NQS^{2-}}}-2\log\frac{[\mathrm{Cl^-}]}{[\mathrm{ZCl}]_o}. \tag{6}$$

The total concentration of zephiramine is considered to be almost the same as that of $[\mathrm{ZCl}]_o$ when the concentration of zephiramine far exceeds that of the reagent. The plots of $\log[\mathrm{HNQSZ}]_o/[\mathrm{HNQS^-}]$ *vs.* $\log[\mathrm{Cl^-}]/[\mathrm{ZCl}]_o$ at pH 3.9 and of $\log[\mathrm{NQSZ_2}]_o/[\mathrm{NQS^{2-}}]$ *vs.* $\log[\mathrm{Cl^-}]/[\mathrm{ZCl}]_o$ at pH 8.9 are shown in Fig. 2. The plots exhibited curves of slope -1 and slope -2 respectively, indicating that the theoretical extraction equilibria were actually established. The extraction exchange constants, as calculated from the ordinate intercept of plots in Fig. 2, are given in Table 1. Considering the values of the extraction exchange constants, it can be assumed that the reagent remains quantitatively in an aqueous phase when the concentrations of chloride are more than 10^3 and 10^2 times that of zephiramine at pH 3.9 and pH 8.9 respectively.

The Compositions of Ion-pairs of Metal–NQS Complexes with Zephiramine. The mole-ratio method and the continuous-variation method are generally used for determining the composition of an extracted ion-pair. However, it is not adequate to apply these methods to determining the ratio of zephiramine to metal when the formation constant of the ion-pair is significantly small, because they occasionally give results in which the apparent number of zephiramine related to metal is much greater than the actual one. Kambara *et al.* have presented a continuous-variation method for three-component systems with a trianglar coordinate to avoid the above-mentioned complication. The present auther has been attempted to apply a slope analysis, which is usually used in a chelate-extraction system, to settle the problem. At pH 3.9, the metal ion, M^{2+}, is extracted into chloroform by forming a water-soluble complex anion with n number of $\mathrm{HNQS^-}$ and by subsequently aggregating with m number of zephiramine, which is necessary to maintain electrical neutrality in the organic phase.

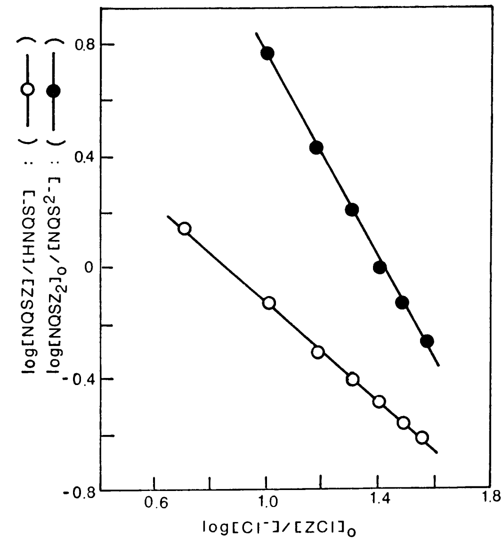

Fig. 2. Relationship between the distribution ratio of 8-hydroxy-7-nitroso-5-quinolinesulfonic acid and log $[\mathrm{Cl^-}]/[\mathrm{ZCl}]_o$.
$[\mathrm{NQS}]=7.9\times10^{-5}$ M, $[\mathrm{ZCl}]=10^{-3}$ M.

For this extraction system, the equation can be written as:

$$\mathrm{M^{2+}}+n\mathrm{HNQS^-}+m\mathrm{ZCl_{(o)}}\rightleftharpoons \mathrm{M(NQS)}_n\mathrm{Z}_{m(o)}+m\mathrm{Cl^-}+n\mathrm{H^+}, \tag{7}$$

where the extraction constant is given by:

$$K_{\mathrm{ex}}=\frac{[\mathrm{M(NQS)}_n\mathrm{Z}_m]_o[\mathrm{Cl^-}]^m[\mathrm{H^+}]^n}{[\mathrm{M^{2+}}][\mathrm{HNQS^-}]^n[\mathrm{ZCl}]_o^m}. \tag{8}$$

The total concentrations of NQS and zephiramine can be expressed as Eqs. 9 and 10:

$$[\mathrm{NQS}]_{\mathrm{total}}=[\mathrm{HNQS^-}]+[\mathrm{HNQSZ}]_o+n[\mathrm{M(NQS)}_n\mathrm{Z}_m]_o, \tag{9}$$

$$[\mathrm{Z}]_{\mathrm{total}}=[\mathrm{ZCl}]_o+[\mathrm{HNQSZ}]_o+m[\mathrm{M(NQS)}_n\mathrm{Z}_m]_o. \tag{10}$$

The distribution ratio of metal between the two phases is given as:

$$D=\frac{[\mathrm{M(NQS)}_n\mathrm{Z}_m]_o}{[\mathrm{M^{2+}}]}. \tag{11}$$

By introducing Eq. 11 to Eq. 8, the following expression is derived:

$$\log D=\log K_{\mathrm{ex}}+n\mathrm{pH}+m\log\frac{[\mathrm{ZCl}]_o}{[\mathrm{Cl^-}]}+n\log[\mathrm{HNQS^-}]. \tag{12}$$

The ratio of metal to zephiramine is obtained as follows. When the concentration of both NQS and zephiramine are sufficiently excessive against that of the metal ion, the third term of Eqs. 9 and 10 can be omitted. When the amount of chloride ions present is more than 70 times that of zephiramine, the second terms of Eqs. 9 and 10 become negligible, because $K^{\mathrm{Cl}^-}_{\mathrm{HNQS}^-}$ is given as 7.08 by Eq. 3. Under these conditions, $[\mathrm{HNQS}^-]$ and $[\mathrm{ZCl}]_o$ can be regarded as $[\mathrm{NQS}]_{\mathrm{total}}$ and $[\mathrm{Z}]_{\mathrm{total}}$ respectively.

Therefore, Eq. 12 can be rewritten as 13 when $[\mathrm{Cl}^-]_{\mathrm{total}} > [\mathrm{Z}]_{\mathrm{total}} \approx [\mathrm{NQS}]_{\mathrm{total}} \gg [\mathrm{M}]_{\mathrm{total}}$:

$$\log D = \log K_{\mathrm{ex}} + n\mathrm{pH} + m\log\frac{[\mathrm{Z}]_{\mathrm{total}}}{[\mathrm{Cl}^-]} + n\log\,[\mathrm{NQS}]_{\mathrm{total}}. \quad (13)$$

This equation represents the plot of $\log D$ *vs.* $\log [\mathrm{Z}]_{\mathrm{total}}/[\mathrm{Cl}^-]$, with a slope corresponding to the ratio of metal to zephiramine under the conditions of a constant pH and a constant NQS concentration. The plots of $\log D$ *vs.* $\log\,[\mathrm{Z}]_{\mathrm{total}}/[\mathrm{Cl}^-]$ for nickel(II) and copper(II) are shown in Fig. 3. As is evident from Fig. 3, the plots gave linear curves with a slope of 2 for nickel(II) and copper(II) in the anticipated ranges. This result indicates that the ratio of metal to zephiramine is 1:2 in each system.

Similarly, the ratio of metal to NQS is obtained as follows. By introducing Eq. 3 to Eq. 12, the following expression is derived:

$$\log D = \log K_{\mathrm{ex}} - m\log K^{\mathrm{Cl}^-}_{\mathrm{HNQS}^-} + n\mathrm{pH} + m\log\,[\mathrm{HNQSZ}]_o + (m-n)\log\,[\mathrm{HNQS}^-]. \quad (14)$$

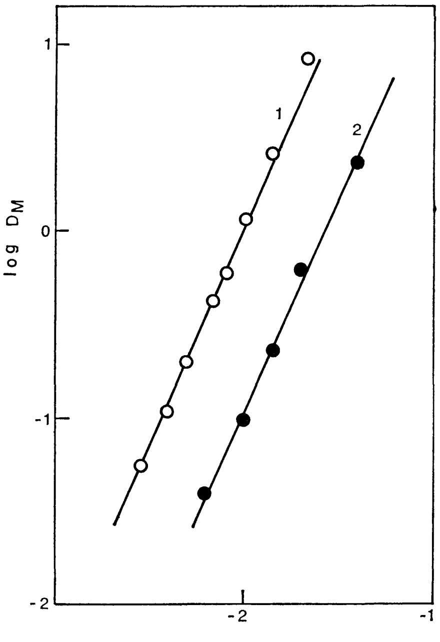

Fig. 3. Relationship between $\log D_{\mathrm{M}}$ and $\log\,[\mathrm{Z}]_{\mathrm{total}}/[\mathrm{Cl}^-]$.
$[\mathrm{NQS}] = 6.32\times10^{-4}$ M, $[\mathrm{ZCl}]_{\mathrm{total}} = 10^{-3}$ M, pH=3.9. 1: $[\mathrm{Ni}] = 3.40\times10^{-5}$ M, 2: $[\mathrm{Cu}] = 3.15\times10^{-5}$ M.

As the terms of $[\mathrm{HNQS}^-]$ and $[\mathrm{M(NQS)}_n\mathrm{Z}_m]_o$ in Eq. 9 can be neglected when the concentration of a ligand is sufficiently in excess against that of the metal ion and when moreover, the concentration of zephiramine exceeds that of the ligand, namely, $[\mathrm{Z}]_{\mathrm{total}} > [\mathrm{NQS}]_{\mathrm{total}} \gg [\mathrm{M}]_{\mathrm{total}}$, $[\mathrm{HNQSZ}]_o$ can be regarded as $[\mathrm{NQS}]_{\mathrm{total}}$. Considering the electrical neutrality of the ion-pair, the numbers of zephiramine and ligand seem to coincide in this system.

Then, supposing $m=n$, Eq. 14 can be rewritten as follows:

$$\log D = \log K_{\mathrm{ex}} - m\log K^{\mathrm{Cl}^-}_{\mathrm{HNQS}^-} + n\mathrm{pH} + m\log\,[\mathrm{NQS}]_{\mathrm{total}}. \quad (15)$$

This equation means that a plot of $\log D$ *vs.* pH gives a slope corresponding to the ratio of metal to the HNQS^- of the extracted complex. The plots of $\log D$ *vs.* pH for nickel(II) and copper(II) at pH 3.9 are shown in Fig. 4. The fact that these plots give curves with a slope of 2 for both the metals indicates an M:NQS ratio of 1:2 in this extraction system. These results agree well with those obtained by the mole-ratio method, and in combination with the results presented above, they indicate that the composition of extracted complexes in the presence of zephiramine is M:NQS:Z=1:2:2. The composition of the precipitated complexes in the aqueous phase,

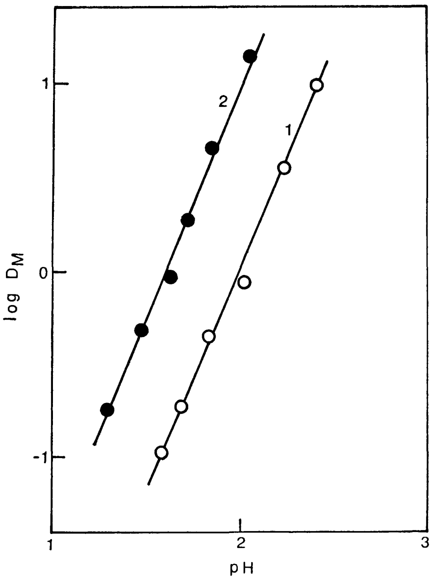

Fig. 4. Relationship between $\log D_{\mathrm{M}}$ and pH.
$[\mathrm{NQS}] = 1.58\times10^{-3}$ M, $[\mathrm{ZCl}]_{\mathrm{total}} = 10^{-2}$ M. 1: $[\mathrm{Ni}] = 3.40\times10^{-5}$ M, 2: $[\mathrm{Cu}] = 3.15\times10^{-5}$ M.

Table 1. Exchange-equilibrium constants and extraction constants for 8-hydroxy-7-nitroso-5-quinolinesulfonic acid($\mathrm{H_2NQS}$) and its metal complexes (Z; Zephiramine)

	λ_{max}/nm	Molar absorptivity/$\mathrm{l\ mol^{-1}\ cm^{-1}}$	$\log K^{m\mathrm{Cl}^-}_{\mathrm{A}^{m-}}$	$\log K_{\mathrm{ex}}$
HNQS	390	2.9×10^3	0.85	—
$\mathrm{NQSZ_2}$	440	5.3×10^3	1.42	—
$\mathrm{Ni(NQS)_2Z_2}$	460	2.6×10^4	4.14	3.40
$\mathrm{Cu(NQS)_2Z_2}$	455	2.5×10^4	3.16	4.10

however, was reported to be M:NQS=1:1 on the basis of the results of the IR spectra and elemental analysis, according to Aly *et al.*[4] Noriki *et al.*[5] have stated that zephiramine has the effect of changing a coordination-unsaturated chelate to an extractable coordination-saturated chelate by accelerating the replacement of water molecules with ligands in the case of magnesium oxinate. It can, therefore, be presumed that zephiramine has a similar effect in the case of NQS complexes.

The absorption maxima, the molar absorptivities, and the exchange-equilibrium constants of the extracted ion-pair complexes are listed in Table 1.

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