1810 *Bull. Chem. Soc. Jpn.*, ***78***, *1810–1813 (2005)*

# Comparison of 8-Quinolinol Derivatives as Carriers for the Collection of Heavy Metals with Emulsion Globules

**Hiroaki Matsumiya,* Ryohei Ohkouchi, and Masataka Hiraide**

Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8603

Received March 28, 2005; E-mail: h-matsu@numse.nagoya-u.ac.jp

A series of 8-quinolinol derivatives has been examined as carriers for the collection of heavy metals with water-in-oil emulsion globules. The emulsion was prepared by dissolving 50 µmol of 8-quinolinol derivative and 30 mg of Span-80 (sorbitan monooleate) in 2.0 $cm^3$ of toluene and vigorously mixing with 0.50 $cm^3$ of 1.0 $mol\,dm^{-3}$ hydrochloric acid by ultrasonic irradiation. The resulting emulsion was gradually injected into 25 $cm^3$ of sample solution [containing 0.10 µg each of Fe(III), Co(II), Ni(II), Cu(II), Cd(II), and Pb(II)] at pH 4–8 and dispersed by stirring for 10 min as numerous tiny globules. When working with the parent compound, 8-quinolinol, Fe(III), Co(II), Ni(II), Cu(II), and Cd(II) were effectively transported through the toluene layer into the internal aqueous phase of the emulsion. However, Pb(II) was not transported at all. The derivatives of 5,7-dichloro-, 2-methyl-, and 5-octyloxymethyl-8-quinolinol were not useful for the simultaneous collection of the heavy metals. On the other hand, Kelex-100 (7-dodecenyl-8-quinolinol) allowed a nearly quantitative (more than 90%) collection of all the metals at pH 7–8. The effects of the substituents on the metal-collection efficiency are discussed in terms of the acidity and hydrophobicity of the carriers.

Water-in-oil (w/o) emulsion globules offer a unique separation technique, sometimes called the emulsion liquid membrane method.[1,2] Typically, a w/o emulsion containing a carrier (e.g., hydrophobic chelating agent) is dispersed in an aqueous solution to cause mass-transfer between the external and internal aqueous phases through the oil layer. Therefore, the emulsion method enables one to perform both extraction and back-extraction more easily and rapidly than the conventional liquid–liquid extraction method. In addition, a higher concentration factor is obtainable because the desired substances can be collected into the tiny aqueous droplets in the emulsion. In spite of these potential advantages, the literature describing the analytical application of the emulsion method is rather scarce.[3–6]

In our laboratory, the emulsion method has been studied from the viewpoint of trace analysis.[7–14] As a part of such efforts, we have recently applied the emulsion method to the preconcentration of trace heavy metals, e.g., Co(II), Ni(II), Cu(II), and Cd(II), in seawater using 8-quinolinol as a carrier.[13] The simultaneous collection required the adjustment of the sample pH to 8.5 so as to ensure complexation of the desired metals with the carrier. However, a lower pH is more favorable because of the instability of the emulsion in alkaline solutions.[13] Therefore, a carrier capable of working under acidic or neutral pH conditions is desirable for the emulsion method.

In the present study, a systematic examination of carriers has been conducted, by taking a series of 8-quinolinol derivatives as an example (Fig. 1), since such an examination should provide useful information for carrier-designing. The results revealed that Kelex-100 (7-dodecenyl-8-quinolinol) is the most promising carrier for the multielement collection of trace heavy metals [e.g., Fe(III), Co(II), Ni(II), Cu(II), Cd(II), and Pb(II)] under neutral pH conditions.

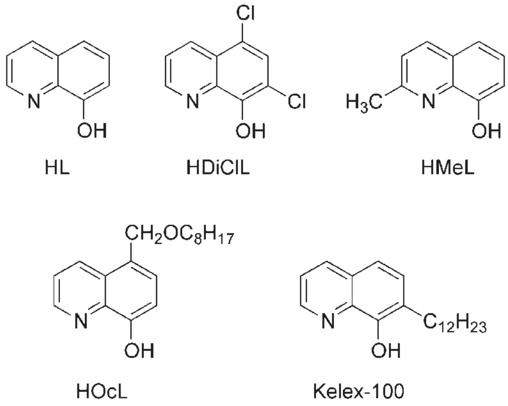

Fig. 1. Structures of 8-quinolinol and its derivatives.

## Experimental

**Apparatus.** A Perkin-Elmer AAnalyst 600 graphite-furnace atomic absorption spectrometer equipped with a Zeeman-effect background corrector was used for the determination of heavy metals under the following furnace operating conditions: The graphite tube was warmed for 1 s to 110 °C and held for 15 s. The tube was further heated for 15 s to 130 °C and held for 15 s; it was then heated for 10 s to a pyrolysis temperature of 500 °C and held for 20 s. The tube was quickly heated to atomization temperatures of 2100 °C (Fe), 2400 °C (Co), 2300 °C (Ni), 2000 °C (Cu), 1500 °C (Cd), or 1600 °C (Pb) and held for 5 s. Clean-up was done at 2450 °C for 3 s. The wavelengths used were 248.3 nm (Fe), 242.5 nm (Co), 232.0 nm (Ni), 324.8 nm (Cu), 228.8 nm (Cd), and 283.3 nm (Pb). Hollow-cathode lamps were operated at 30 mA (Fe and Co), 25 mA (Ni), 15 mA (Cu), 6 mA (Cd), and 10 mA (Pb).

Published on the web October 4, 2005; DOI 10.1246/bcsj.78.1810

A Branson Model 450 Sonifier II ultrasonic homogenizer (20 kHz, 80 W) equipped with a 12-mm diameter titanium cylindrical transducer was used for the emulsification. Separation procedures were carried out in a Hitachi ECV-843 BY clean bench.

**Reagents.** 8-Quinolinol (HL, Nacalai Tesque), 5,7-dichloro-8-quinolinol (HDiClL, Tokyo Kasei), 2-methyl-8-quinolinol (HMeL, Wako Pure Chemicals), and 5-octyloxymethyl-8-quinolinol (HOcL, Wako Pure Chemicals) were used without further purification. Kelex-100 was kindly gifted by Prof. Katsutoshi Inoue (Department of Applied Chemistry, Saga University), and it was purified as described in the literature.[15] Working solutions of the carriers (25 mM) were prepared by dissolving the respective HL derivatives in toluene ($1\ \mathrm{M} = 1\ \mathrm{mol\,dm^{-3}}$). The emulsifier used was Span-80 (extra pure reagent grade, Nacalai Tesque). Standard solutions of heavy metals ($10\ \mu\mathrm{g\,cm^{-3}}$ in 0.1 M nitric acid) were prepared from commercial standard solutions (Nacalai Tesque). The following buffers were used to adjust the sample pH: formic acid–NaOH (pH 3.5–4.3), acetic acid–NaOH (pH 4.3–5.5), 2-morpholinoethanesulfonic acid (MES)–NaOH (pH 5.5–6.5), and 3-morpholinopropanesulfonic acid (MOPS)–NaOH (pH 6.5–8.0).

All reagents used were of analytical reagent grade, unless otherwise stated. Water was purified with a Millipore Milli-Q Gradient water system.

**Procedure.** In a 20-cm$^3$ glass vial were placed 30 mg of Span-80, 2.0 cm$^3$ of carrier solution, and 0.50 cm$^3$ of 1.0 M HCl. The mixture was agitated ultrasonically for 15 s to form a w/o emulsion.

A 25-cm$^3$ volume of sample solution (containing 0.10 µg each of heavy metals and 0.25 mmol of pH buffer) was placed in a 50-cm$^3$ glass beaker. While stirring the sample solution with a magnetic stirrer using a 30-mm stirring bar at 480 rpm, the emulsion was gradually injected and dispersed as numerous tiny globules (typical diameters of 0.01–0.1 mm). After stirring for 10 min, the solution was transferred to a 50-cm$^3$ separating funnel and left to stand for 3 min to float the emulsion globules completely. The underlying aqueous phase was removed by suction, and the remaining emulsion was transferred to a 10-cm$^3$ test tube.

The emulsion was heated on a water bath (ca. 90 °C) to segregate the aqueous and organic phases. All the aqueous phase was collected in a 1-cm$^3$ volumetric flask with the aid of a Pasteur pipette, and then diluted to the mark with water. A 10-mm$^3$ aliquot of the solution (after dilution, if necessary) was subjected to the determination of heavy metals by graphite-furnace atomic absorption spectrometry (GFAAS); the determination of Cd was performed with the addition of 0.4 µg of Mg and 10 µg of $NH_4H_2PO_4$ as matrix modifiers. The measurement was repeated three times, and the obtained signals were averaged. Calibration graphs were constructed using 0.5 M HCl containing metals of interest at $\mathrm{ng\,cm^{-3}}$ levels.

## Results and Discussion

**8-Quinolinol.** HL is characterized by its wide reactivity with various heavy metals,[16] and is utilized for the multielement preconcentration of heavy metals in water samples.[17–20] In the present study, therefore, HL and its derivatives were employed as carriers. Iron(III), cobalt(II), nickel(II), copper(II), cadmium(II), and lead(II) were taken as examples of trace heavy metals to be collected, because of their importance in environmental studies. First, the effect of the pH on the recovery of heavy metals was investigated with the parent compound HL. The emulsion was prepared from toluene, HCl, and Span-80 (sorbitan monooleate) in a similar manner to that described in our previous report.[13] The emulsion was added to the sample solution and dispersed by stirring for 10 min, which was the optimal stirring time (not only for HL, but also for its derivatives tested later). The heavy metals collected into the internal aqueous phase were determined by GFAAS to calculate the recoveries. In some experiments, the external aqueous phase (sample solution) and the organic phase were also analyzed by GFAAS to confirm that the sum of the amounts of metals found in the internal, external, and organic phases coincided with the initial amounts of metals.

As shown in Fig. 2, the nearly quantitative (more than 90%) recoveries were obtained for Fe(III), Co(II), Ni(II), Cu(II), and Cd(II) under a slightly alkaline condition, pH 8. Although lower pH is more favorable because of the instability of the emulsion in alkaline solutions, the recoveries of Co(II), Ni(II), and Cd(II) decreased with decreasing the pH. In addition, Pb(II), a highly toxic heavy metal, was not collected at any pH region tested. The multielement collection of heavy metals is of importance in environmental analysis; hence, several HL derivatives were examined for improving the metal-collection efficiency.

**5,7-Dichloro-8-quinolinol.** The introduction of halogens into the HL molecule facilitates deprotonation of the resulting derivatives; hence, they react with metals generally in a more acidic medium than the parent compound, HL.[16] Therefore, a dichlorinated derivative, HDiClL, was examined as a carrier. As shown in Table 1, the acidity of HDiClL is stronger than that of HL by 2 p$K_a$ units.[16]

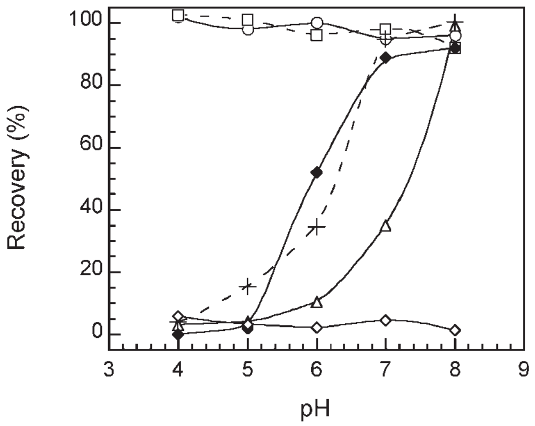

Fig. 2. Collection of 0.10 µg each of Fe(III) (□), Co(II) (△), Ni(II) (◆), Cu(II) (○), Cd(II) (+), and Pb(II) (◇) in 25 cm$^3$ of water with HL-impregnated emulsion.

Table 1. Some Chemical Properties of 8-Quinolinol Derivatives

| | p$K_{a,NH}$ | p$K_{a,OH}$ | log $K_D$[a)] |
|---|---|---|---|
| HL[b)] | 5.0 | 9.7 | 2.7 |
| HDiClL[b)] | 2.9 | 7.5 | 3.8 |
| HMeL[b)] | 5.8 | 10.0 | 3.4 |
| HOcL[c)] | —[e)] | 10.9 | 5.1 |
| Kelex-100[d)] | —[e)] | 10.4 | 5.5 |

a) Chloroform–water. b) Ref. 16. c) Ref. 21. d) Ref. 15. e) Not given.

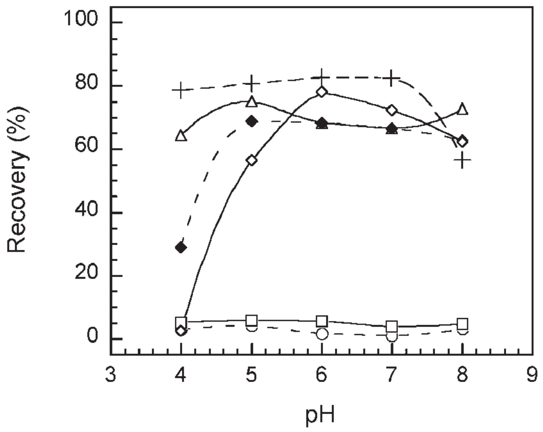

Fig. 3. Collection of 0.10 μg each of Fe(III) (□), Co(II) (△), Ni(II) (◆), Cu(II) (○), Cd(II) (+), and Pb(II) (◇) in 25 $cm^3$ of water with HDiClL-impregnated emulsion.

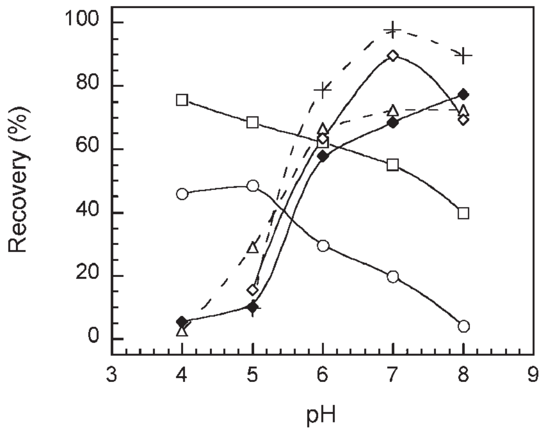

Fig. 5. Collection of 0.10 μg each of Fe(III) (□), Co(II) (△), Ni(II) (◆), Cu(II) (○), Cd(II) (+), and Pb(II) (◇) in 25 $cm^3$ of water with HOcL-impregnated emulsion.

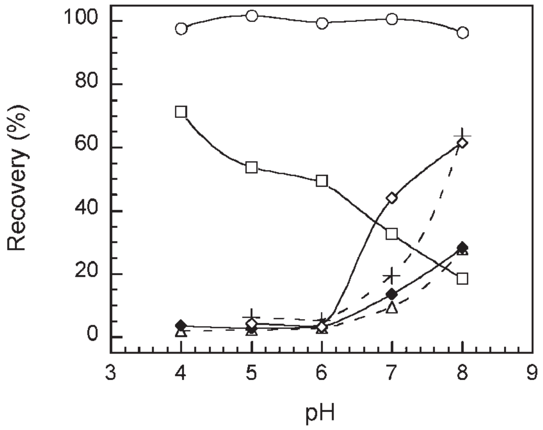

Fig. 4. Collection of 0.10 μg each of Fe(III) (□), Co(II) (△), Ni(II) (◆), Cu(II) (○), Cd(II) (+), and Pb(II) (◇) in 25 $cm^3$ of water with HMeL-impregnated emulsion.

Figure 3 shows the recoveries of heavy metals as a function of the pH. Improved recoveries were obtained for Co(II), Ni(II), Cd(II), and Pb(II) under acidic or neutral pH conditions, though the recoveries were not satisfactory (80% or less). On the other hand, the percentages of the metals removed from the sample solution were higher than the recoveries; for example, more than 95% of Co(II), Ni(II), Cd(II), and Pb(II) were removed from the sample solution at pH 6 and 7. These results indicate that the metal–HDiClL chelates were too stable to release the metals into the internal aqueous phase, hence providing the insufficient recoveries. For Fe(III) and Cu(II), the recoveries were also not satisfactory, almost zero.

**2-Methyl-8-quinolinol.** HMeL was taken as an example of a carrier being more basic than the parent compound, HL. As shown in Fig. 4, HMeL allowed the quantitative recovery of Cu(II). However, the recoveries of the other metals were insufficient; complete complexation required alkaline pH conditions due to the relatively high basicity of HMeL.

**5-Octyloxymethyl-8-quinolinol.** When working with the above-mentioned carriers (HL, HDiClL, and HMeL), the aqueous phase segregated from the emulsion was tinged with yellow. This suggests that the carriers were considerably distributed into the internal aqueous phase (1.0 M HCl). Therefore, the net concentration of the carriers in the organic phase was somewhat lower than the initial concentration, which would lower the metal-transport efficiency. For avoiding a decrease in the carrier-concentration, more hydrophobic HL derivatives seem to be promising.

An alkyloxymethylated derivative, HOcL, is characterized by its high hydrophobicity: the $\log K_{\rm D}$ value (5.1)[21] is much greater than those of HL (2.7),[16] HDiClL (3.8),[16] and HMeL (3.4).[16] It has also been reported that HOcL is hardly distributed into acidic aqueous solutions.[22] In spite of the fact that HOcL is more basic than HMeL (Table 1), improved recoveries were obtained for Co(II), Ni(II), Cd(II), and Pb(II) under neutral pH conditions (Fig. 5), probably because leakage of the carrier into the internal aqueous phase was effectively prevented. However, HOcL was not useful for the simultaneous collection of the metals at any pH region tested.

**Kelex-100.** Kelex-100 is another hydrophobic HL derivative ($\log K_{\rm D} = 5.5$),[15] in which a dodecenyl group is introduced into the 7-position. The basicity of Kelex-100 lies between those of HL and HOcL, as shown in Table 1. Isshiki et al. reported that the extraction behaviors of heavy metals with Kelex-100 were similar to those with HL, and they utilized Kelex-100 for the multielement preconcentration of heavy metals.[23] As shown in Fig. 6, Kelex-100 allowed the simultaneous collection of all the metals tested, viz., Fe(III), Cu(II), Co(II), Ni(II), Cd(II), and Pb(II), in satisfactory yields (more than 90%) at pH 7–8.

The higher metal-collection efficiency of Kelex-100 than HOcL seems to be ascribed to the lower basicity and higher hydrophobicity of Kelex-100. The difference in the location of the hydrophobic substituent may also be responsible, at least in part, for the difference in the metal-collection efficiency. The hydrophobic substituent of HOcL is located at the opposite side of the chelating site, whereas that of Kelex-100 is adjacent to the chelating site. This likely affects the chelate-formation and/or dissociation processes at the oil–water interface.

In conclusion, Kelex-100, a hydrophobic 8-quinolinol derivative with a dodecenyl group at the 7-position, was found to be a promising carrier for the multielement collection of trace

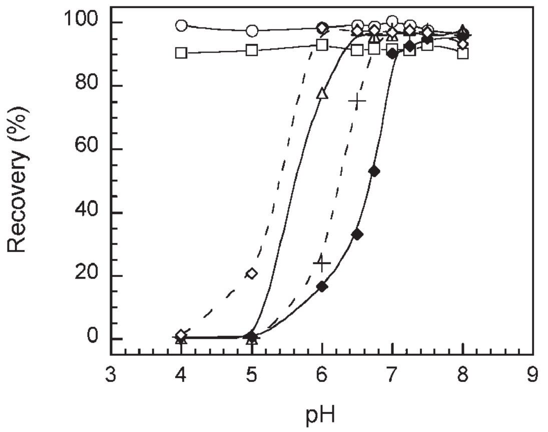

Fig. 6. Collection of 0.10 μg each of Fe(III) (□), Co(II) (△), Ni(II) (◆), Cu(II) (○), Cd(II) (+), and Pb(II) (◇) in 25 cm$^3$ of water with Kelex-100-impregnated emulsion.

heavy metals under neutral pH conditions. The revealed high performance of the Kelex-100-impregnated emulsion encourages its analytical use as a preliminary separation and/or concentration vehicle for water analysis, which is underway in our laboratory.

The authors are grateful to Prof. Katsutoshi Inoue (Department of Applied Chemistry, Saga University) for generously providing a sample of Kelex-100.

## References

1 D. K. Schiffer, A. Hochhauser, D. F. Evans, and E. L. Cussler, *Nature*, **250**, 484 (1974).

2 A. M. Sastre, A. Kumar, J. P. Shukla, and R. K. Singh, *Sep. Purif. Methods*, **27**, 213 (1998).

3 Y. Okamoto, T. Takahashi, K. Isobe, and T. Kumamaru, *Anal. Sci.*, **6**, 401 (1990).

4 Z. Wang, J. Li, J. C. Van Loon, and R. R. Barefoot, *Anal. Chim. Acta*, **252**, 205 (1991).

5 Y. Li, J. C. Van Loon, and R. R. Barefoot, *Fresenius' J. Anal. Chem.*, **345**, 467 (1993).

6 T. Yokoyama, T. Watarai, T. Uehara, K. Mizuoka, K. Kohara, M. Kido, and M. Zenki, *Fresenius' J. Anal. Chem.*, **357**, 860 (1997).

7 M. Hiraide, K. Ishikawa, and H. Kawaguchi, *Fresenius' J. Anal. Chem.*, **356**, 155 (1996).

8 M. Hiraide and K. Hasegawa, *Fresenius' J. Anal. Chem.*, **363**, 261 (1999).

9 M. Hiraide, M. Ogoh, S. Itoh, and T. Kageyama, *Talanta*, **57**, 653 (2002).

10 T. Kageyama and M. Hiraide, *Bunseki Kagaku*, **51**, 741 (2002).

11 T. Kageyama, H. Matsumiya, and M. Hiraide, *Anal. Bioanal. Chem.*, **379**, 1083 (2004).

12 M. Nakao, H. Matsumiya, and M. Hiraide, *Bunseki Kagaku*, **53**, 975 (2004).

13 H. Matsumiya, T. Kageyama, and M. Hiraide, *Anal. Chim. Acta*, **507**, 205 (2004).

14 R. Ohkouchi, H. Matsumiya, and M. Hiraide, *Bunseki Kagaku*, in press.

15 S. P. Bag and H. Freiser, *Anal. Chim. Acta*, **135**, 319 (1982).

16 J. Stary, "The Solvent Extraction of Metal Chelates," Pergamon Press, Oxford (1964), Chap. 5.

17 H. Watanabe, K. Goto, S. Taguchi, J. W. McLaren, S. S. Berman, and D. S. Russell, *Anal. Chem.*, **53**, 738 (1981).

18 R. E. Sturgeon, S. S. Berman, S. N. Willie, and J. A. H. Desaulniers, *Anal. Chem.*, **53**, 2337 (1981).

19 T. Saitoh, T. Ohyama, T. Sakurai, T. Kaise, K. Takamura, Y. Suzuki, and C. Matsubara, *Talanta*, **46**, 541 (1998).

20 H. Ohashi, N. Uehara, and Y. Shijo, *J. Chromatogr., A*, **539**, 225 (1991).

21 H. Kokusen, K. Suzaki, K. Ohashi, and K. Yamamoto, *Anal. Sci.*, **4**, 617 (1988).

22 K. Ohashi, S. Nakata, M. Katsume, K. Nakamura, and K. Yamamoto, *Anal. Sci.*, **1**, 467 (1985).

23 K. Isshiki, F. Tsuji, T. Kuwamoto, and E. Nakayama, *Anal. Chem.*, **59**, 2491 (1987).