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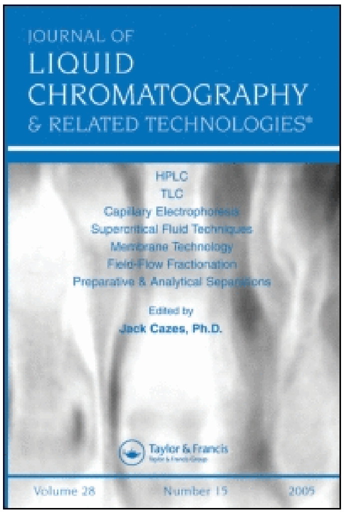

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REVERSED-PHASE CHROMATOGRAPHIC BEHAVIOR OF METAL COMPLEXES WITH 8-HYDROXYQUINOLINE AND ITS DERIVATIVES

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ABSTRACT

Chromatographic behavior of metal complexes with 8-hydroxyquinoline, 5-chloro-8-hydroxyquinoline, and 5,7-chloro-8-hydroxyquinoline in the reversed-phase system has been studied using a variety of organic modifiers. In the acetone modifier system, the capacity factors (k') of the corresponding vanadium(V), nickel(II), and cobalt(III) complexes increased with increasing number of substituted chlorine atoms in the ligands. With acetonitrile-water as the mobile phase, the k' values of the metal 8-hydroxyquinoline complexes decreased with increasing contents of the modifier, depending on the strength of polarity parameters. The k' values, experimentally determined, can be related to the polarity parameters of organic modifiers for tervalent metal ions, but not for monovalent and divalent ions.

INTRODUCTION

Numerous studies have been reported on the reversed-phase liquid chromatographic (RPLC) behavior of solutes with a variety of organic modifiers.[1,2] Some assumptions have been made for the qualitative prediction of retention times for some solutes.[3,4] In general, the RPLC retention obeys the linear relationship between log k', where k' is capacity factor, and volume fraction of organic modifier in the mobile phase. However, methanol and acetonitrile as the modifier are not ideal water-modifier systems where the relationship often exhibites some curvature on the graph.[5] Very little is understood about the relationship between capacity factor and some physico-chemical parameter of different modifiers in the RPLC of metal complexes.[6]

Recently, hydrophobic metal chelates with 8-hydroxyquinoline[7,8] and 4-(2-pyridylazo)resorcinol[9] have been used for the determination of metal ions by the RPLC method. The retention behavior of the metal species has not been clearified systematically, and the modifier to be added to the mobile phase has been selected according to the empirical rules. The optimum chromatographic conditions like pH, the concentration of the chelating agent, and the composition of mobile phase (modifier/water) were chosen by examining the experimental variables. It is very important to know the relationship between capacity factor of metal chelates and physico-chemical property of modifiers because the qualitative predictions of such solutes become possible.

The purpose of this study is to clearify the retention behavior of metal species in the RPLC system. One approach is made using polarity parameter of chosen modifiers and mobile phases for the prediction of capacity factors.[10-13]

EXPERIMENTAL

Apparatus and Reagents

The liquid chromatographic system used consisted of a Tosoh (Tokyo, Japan) Model CCPD pump, a Sanuki (Shiga, Japan) Model SVI-6U7 injector equipped with a 100 μL sample loop, a Shimadzu (Kyoto, Japan) Model SPD-6AV UV-VIS spectrophotometer, and a Shimadzu Model CR-6A data processor. The analytical column was a Tosoh ODS-80TM (4.6 x 150 mm, 5 μm). A Toa Denpa (Saitama, Japan) Model HM-30S pH meter was used for pH measurements.

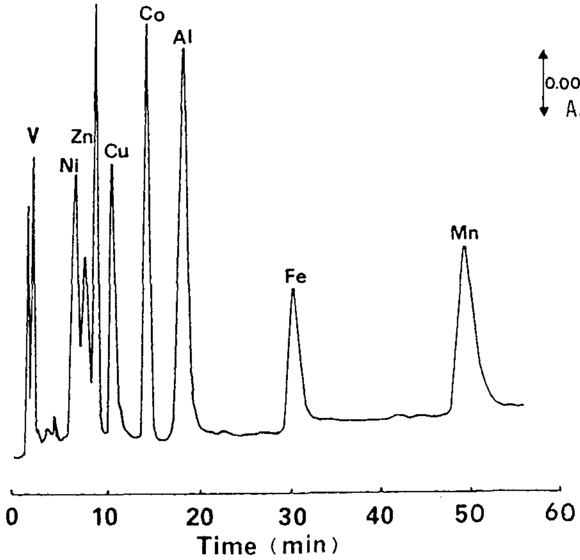

Figure 1. Chromatogram for metal 8-HQ complexes. Eluent: 35/65 (v/v) acetonitrile-0.02 mol/L sodium acetate (pH 7.5);flow rate: 1.0 mL/min; metal ion concentration: 100 ng/mL;injection volume: 100 μL; wavelength for detection: 390 nm.

Such hydroxyquinoline (HQ) compounds as 8-hydroxyquinoline (8-HQ), 5-chloro-8-hydroxyquinoline (5-Cl-8-HQ), and 5,7-dichloro-8-hydroxyquinoline (5-7-Cl-8-HQ) were from Wako Junyaku Kogyo (Tokyo, Japan) and used without purification. Acetonitrile, acetone, tetrahydrofuran, 1,4-dioxane, and other organic solvents as modifiers were of HPLC grade from Nakarai Tesque (Kyoto, Japan).

Metal ion standards of a desired concentration were prepared by dilution of stock 1000 ppm standard solutions for atomic absorption spectrometry. Deionized water was obtained from Millipore Milli-Q water purification system.

Procedure

The metal complexes with 8-HQ or its derivatives were formed by adding 1.0 mL of 0.1 μg/mL metal ion solution to 1.0 mL of 0.02 mol/L 8-HQ solution in pure organic modifier.

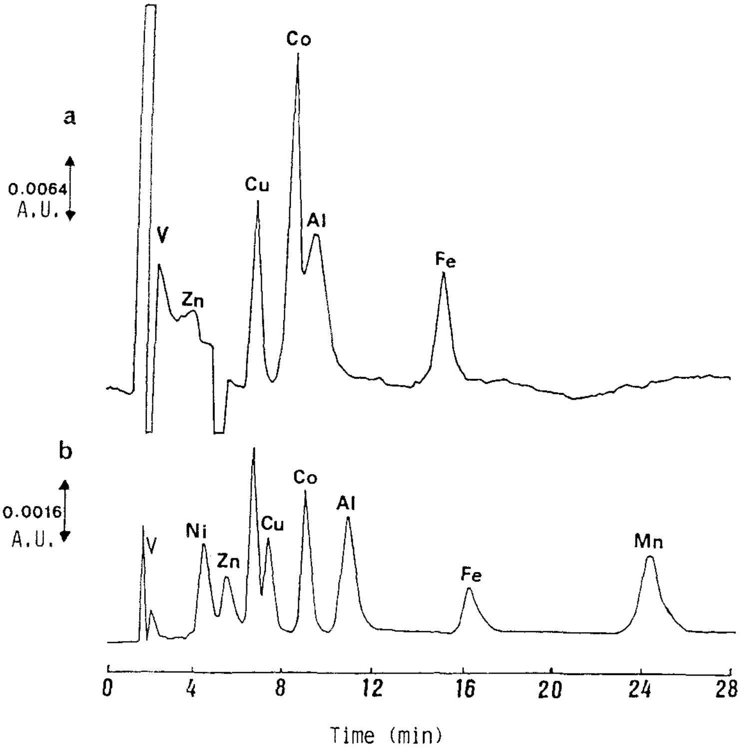

Figure 2. Chromatograms for metal 8-HQ complexes with eluents of pH 3.5(a) and pH 7.5 (b). Eluent: 2/3 (v/v) acetonitrile-0.02 mol/L acetate buffer (pH 7.5 and 3.5); other experimental conditions as in Figure 1.

A 100 μL portion of the resultant solution was injected into the C_{18} column, and eluted with a mixture of organic modifier-0.02 mol/L sodium acetate (pH 7.5) containing 5×10^{-3} mol/L 8-HQ at 1.0 mL/min. The column temperature was kept at 20 ± 0.1°C.

The absorbance of the eluate was monitored with the spectrophotometric detector at 390 nm. The capacity factor (k') was calculated from the formula $k' = (t_r - t_m)/t_m$ where t_r and t_m were the retention time (t_r) of the metal complex and the dead time (t_m) of the column, respectively.

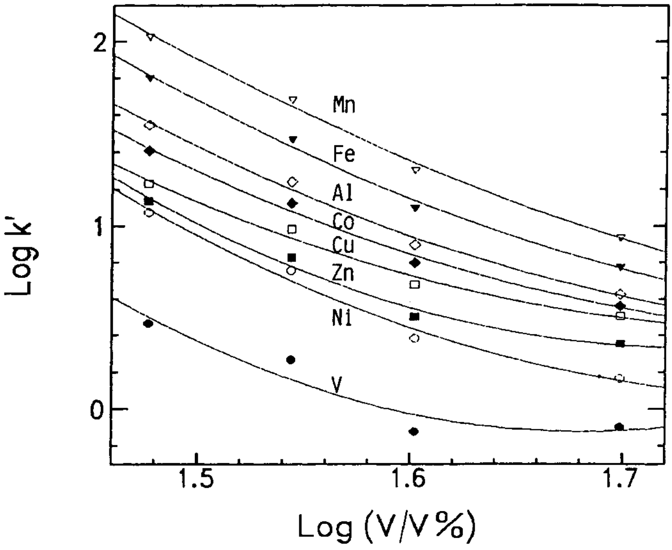

Figure 3. Relationships between capacity factor and volume fraction of acetonitrile in the mobile phase for metal 8-HQ complexes. Experimental conditions as in Figure 1.

Table 1

Comparison of Capacity Factors for Metal Complexes with 8-HQ Derivatives*

Ligand	Capacity Factor		
	Vanadium	Nickel	Cobalt
8-HQ	0.45	1.31	4.50
5-Cl-8-HQ	0.98	5.04	9.92
5-7-Cl-8-HQ	3.97	13.4	29.3

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* Eluent: 3/2 (vv) acetone-0.02 mol/L sodium acetate; other experimental conditions as in Figure 1.

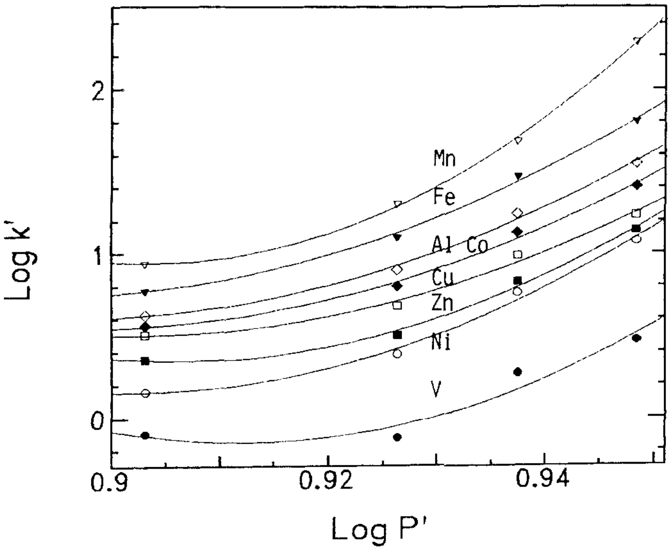

Figure 4. Relationships between capacity factor and polarity parameter for metal 8-HQ complexes. Experimental conditions as in Figure 1.

RESULTS AND DISCUSSION

RPLC Separation of Metal 8-HQ Complexes

A number of metal ions are known to form non-ionic complexes with 8-HQ derivatives in moderately acidic medium. When such metal complexes are introduced to an ODS column under the RPLC conditions, they are retained and give well-separated chromatograms. Methanol and acetonitrile have often been used for organic modifiers of mobile phases. Figure 1 shows a typical elution curve for some metal 8-HQ complexes with a mixture of 35/65 (v/v) acetonitrile-0.02 mol/L sodium acetate as the mobile phase. The k' values of the metal complexes, calculated from the retention times, increased in the order of $VO_2(I) < Ni(II) < Zn(II) < Cu(II) < Co(III) < Al(III) < Fe(III) < Mn(III)$ which coincided with the apparent valencies of the metal ions.

The k' values for $VO_2(I)$, Ni(II), and Co(III) complexes with 5-Cl-8-HQ and 5,7-Cl-8-HQ were obtained with 3:2 (v/v) acetone-0.02 mol/L sodium acetate as the mobile phase, as shown in Table 1. As expected, the capacity factor depended on valency and stability of the complexes: $VO_2(I) < Ni(II)$

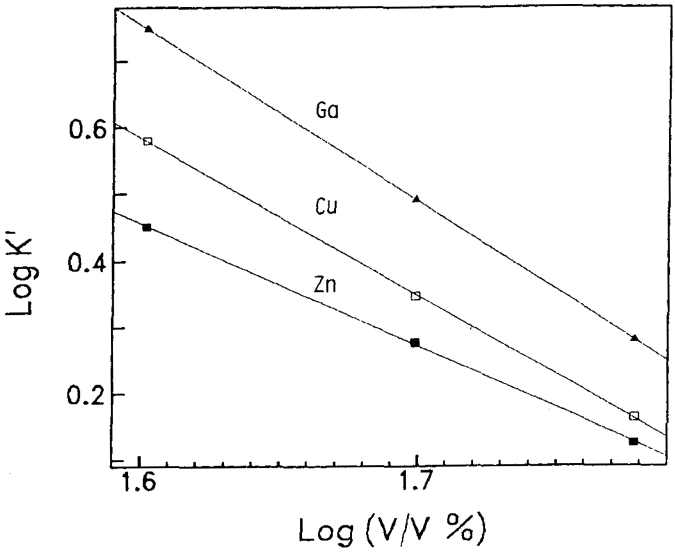

Figure 5. Relationships between capacity factor and volume fraction of tetrahydrofuran in the mobile phase for metal 8-HQ complexes. Eluents: tetrahydrofuran-0.02 mol/L sodium acetate; other experimental conditions as in Figure 1.

<Co(III) and 8-HQ < 5-Cl-8-HQ < 5,7-Cl-8-HQ. It appears that this order concerning k' can also be explained on the basis of the hydrohobic property of the metal complexes. The larger the size of metal complexes, the stronger the hydrohobic interaction between metal species and non-polar ODS functional groups of the column. As a result of a stronger retention, we can get larger k' values in the RPLC system.

Effect of pH of Acetonitrile Mobile Phase on k'

Chromatograms of some metal complexes were recorded with 2:3 (v/v) acetonitrile-0.02 mol/L acetate buffers at pH 3.5 and 7.5 (Figure 2) as mobile phases. Compared to the two chromatograms, the k' values at pH 3.5 were lower than those at pH 7.5.

This result is presumably a result of shielding silanol groups with hydrogen ions on the surface of the ODS column. The nickel(II), cobalt(III) and manganese(III) complexes at pH 3.5 gave no elution peak due to degradation of the species in an acidic medium.

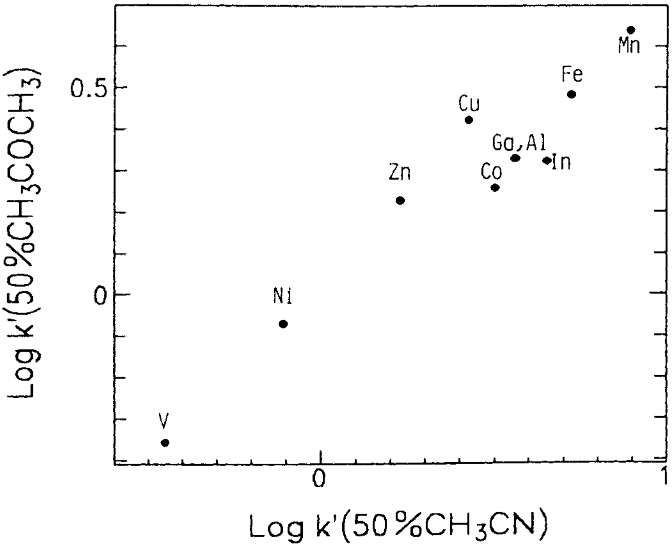

Figure 6. Comparison of capacity factors obtained for acetonitrile and acetone as mobile phases. Eluents: 1/1 (v/v) organic modifer (acetonitrile or acetone)-0.02 mol/L sodium acetate; other experimental conditions as in Figure 1.

Effect of Acetonitrile/Water Ratio of the Mobile Phase on k'

When the content of acetonitrile in the mobile phase increased, the k' values for the metal complexes with 8-HQ decreased as shown in Figure 3. The relationships between k' and volume fraction of acetonitrile exhibited substantially good linearity for tervalent metal ions but somewhat curvature for the other ions. It appears that the acetonitrile/water mobile phase is an ideal binary solvent mixture of reversed-phase chromatography for specified conditions.

One approach relating to retention of metal 8-HQ complexes as a function of polarity parameter (P) of the mobile phase has been attempted in this study. The polarity parameters of acetonitrile/water mixtures were obtained by calculating from the formula $P' = xP_1 + yP_2$, where P_1 (5.8) and P_2 (10.2) are polarity parameters of pure acetonitrile and water, and x and y are volume fractions of acetonitrile and water, respectively. The relationships between log k' and log P' for the metal ions were best fitted by quadratic equations as shown in Figure 4.

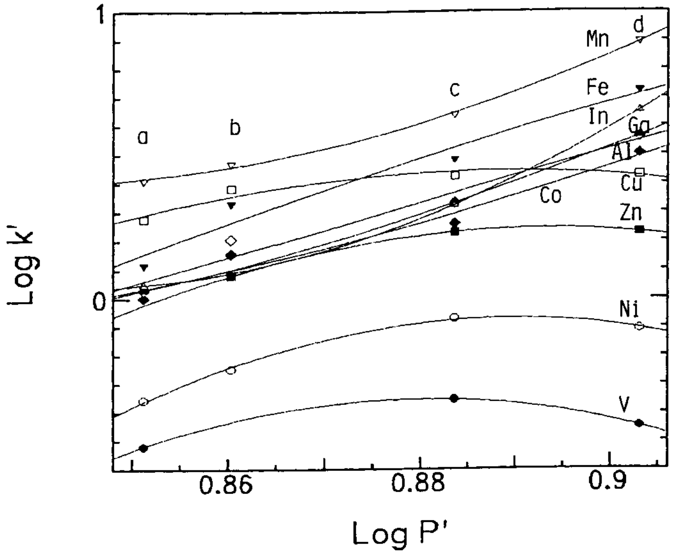

Figure 7. Relationships between capacity factor and polarity parameter for metal 8-HQ complexes. Eluents:1/1 (v/v) organic modifier-0.02 mol/L sodium acetate; a:tetrahydrofuran; b:1,4-dioxane; c:acetone; d:acetonitrile; other experimental conditions as in Figure 1.

Relationship Among Organic Modifiers

In addition to acetonitrile, the k' values for the 8-HQ complexes were determined with tetrahydrofuran, acetone, ethanol, propanol and 1,4-dioxane as organic modifies. Among them, tetrahydrofuran and ethanol exhibited linear relationshps between log k' and volume fraction of the modifier. Figure 5 shows the relationship between log k' and logarithm of volume fraction of detrahydrofuran

The relationship between the two modifiers was investigated using the k' values obtained with 1:1 organic modifier-0.02 mol/L sodium acetate mobile phase. Relatively good linearity was found between acetonitrile and acetone as shown in Figure 6, but there was a poor relationship between acetonitrile and the other modifiers. In the case of both organic modifiers, similar retention behavior is expected for the reversed-phase chromatography of the metal 8-HQ complexes.

Finally, the dependence of the k' values for metal 8-HQ complexes on P' of organic modifiers was investigated. Figure7 shows plots of log k' against log P' where 1/1 (v/v) tetrahydrofuran, 1,4-dioxane, acetone or acetonitrile-0.02 mol/L sodium acetate was used as the mobile phase. It is clear that there are many differences among the metal ions in the curvature of the plots shown in Figure 7. That is, the k' values of the acetone mobile phase were the highest for the mono- and divalent metal ions, while acetonitrile exhibited the strongest retention for the tervalent metal ions. For such higher hydrohobic solutes, the retention on the ODS column becomes stronger in the order of tetrahydrofuran > 1,4-dioxane > acetone > acetonitrile, depending on the polarity parameters of the organic modifiers. We have examined the relationships between k' and such parameters as solubility parameter, dielectric constant, or ET index[1] (a spectroscopic function) with respect to organic modifiers. No clear relationship was found except for polarity parameter. We, therefore, can conclude that both hydrohobic property of solutes and polarity parameter of organic modifiers determine the retention of solutes in the reversed-phase chromatography.

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