Notes

"Substituent on Benzenesulfonyl Group" Effect in Use of 8-Benzenesulfonamidoquinoline Derivatives as Chelate Extractant

Naoki Hirayama,*† **Noriko Sugisaka,**** **Junko Taga,**** **Syunichi Oshima,*****
and Takaharu Honjo*

 **Department of Chemistry, Faculty of Science, Kanazawa University,*
  Kakuma-machi, Kanazawa 920–1192, Japan
 ***Division of Material Chemistry, Graduate School of Natural Science and Technology,*
  Kanazawa University, Kakuma-machi, Kanazawa 920–1192, Japan
****Division of Basic Sciences, Graduate School of Natural Science and Technology,*
  Kanazawa University, Kakuma-machi, Kanazawa 920–1192, Japan

"Substituent on benzenesulfonyl group" effect of 8-benzenesulfonamidoquinoline [*N*-(8-quinolyl)benzenesulfonamide, Hbsq] as bidentate chelate extractant for divalent metal cations was investigated with using Hbsq and its eight derivatives. Introduction of electron-withdrawing substituent on the benzenesulfonyl group in Hbsq enhanced the extractability that originated from its inductive effect. Furthermore, *a* bulky substituent on *an ortho*-position of the benzenesulfonyl group resulted in no steric effect in extraction, whereas the existence of *two* substituents on *each ortho*-position caused lower extraction performance due to steric hindrance.

In chelate extraction, an extractant should have at least one donor atom having negative charge to form a neutral (extractable) complex with a target metal cation. In general, only $-O^-$ and $-S^-$ have been used as the negatively charged donor. Although an amino group (primary or secondary) has too low acidity to form $>N^-$, sulfonamide group ($-NH-SO_2R$) has acidity comparable to that of phenolic-OH.[1–3] From this viewpoint, several researchers have studied the extraction nature of 8-sulfonamidoquinoline derivatives,[4–10] which are sulfonamide-type analogues of 8-hydroxyquinoline (Hox, a well-known and well-researched bidentate monoanionic extractant).

8-Benzenesulfonamidoquinoline [*N*-(8-quinolyl)benzene-sulfonamide, Hbsq] has two aromatic units such as a quinoline ring and a benzene ring (in benzenesulfonyl group). However, there is no report concerning a "distant" substituent effect derived on the latter in the chelate extraction, whereas the "close" substituent effect on the former in Hox has been studied widely. In this research, we investigated the "substituent on benzenesulfonyl group" effect of Hbsq as chelate extractant for divalent metal cations using the following eight derivatives: 8-(*p*-toluenesulfonamido)quinoline [4-methyl-*N*-(8-quinolyl)-benzenesulfonamide, H(*p*-Me)bsq], 8-(2,4,6-trimethylbenzenesulfonamido)quinoline [2,4,6-trimethyl-*N*-(8-quinolyl)benzenesulfonamide, H(2,4,6-Me₃)bsq], 8-(*p-tert*-butylbenzenesulfonamido)quinoline [4-(dimethylethyl)-*N*-(8-quinolyl)benzenesulfonamide, H(*p-t*-Bu)bsq], 8-(*p*-chlorobenzenesulfonamido)quinoline [4-chloro-*N*-(8-quinolyl)-

benzenesulfonamide, H(*p*-Cl)bsq], 8-(*o*-, *m*-, or *p*-nitrobenzenesulfonamido)quinoline [2-, 3-, or 4-nitro-*N*-(8-quinolyl)benzenesulfonamide, H(*o*-, *m*-, or *p*-NO₂)bsq] and 8-(2,4-dinitrobenzenesulfonamido)quinoline [2,4-dinitro-*N*-(8-quinolyl)benzenesulfonamide, H(2,4-(NO₂)₂)bsq]. Figure 1 shows the chemical structures of these 9 extractants. As a result, it was found that introduction of electron-withdrawing substituent on the benzenesulfonyl group in Hbsq enhances the extractability that originated from its inductive effect. Furthermore, it was found that *a* bulky substituent on *an ortho*-position of the benzenesulfonyl group results in no steric effect
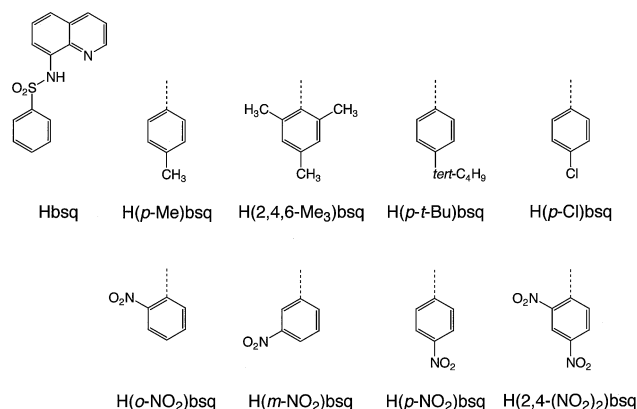

Fig. 1   Chemical structures of Hbsq and its derivatives that were used in this study as extractants.

† To whom correspondence should be addressed.
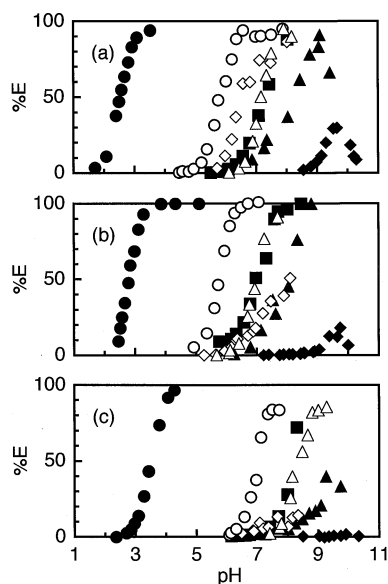E-mail: hirayama@cacheibm.s.kanazawa-u.ac.jp

Fig. 2   Plots of the extracted ratios (%E) for some divalent metals as a function of the aqueous phase pH equilibrated with organic phase (chloroform) in Hbsq (A), H(p-Me)bsq (B) and H(2,4,6-Me$_3$)bsq (C) systems. Initial ligand concentration in chloroform was 1×10^{-3} mol dm^{-3}. ◆, Mn^{2+}; ■, Co^{2+}; ▲, Ni^{2+}; ●, Cu^{2+}; ○, Zn^{2+}; △, Cd^{2+}; ◇, Pb^{2+}.

Fig. 3   Plots of log $D(1 + \beta_1[OH^-] + \beta_2[OH^-]^2)$ for Cu^{2+} and Zn^{2+} into chloroform in H(p-Me)bsq system as a function of the aqueous phase pH (A) and those as a function of the logarithmic concentration of H(p-Me)bsq in organic phase (B). Initial concentration of H(p-Me)bsq was 1×10^{-3} mol dm^{-3} on (A), and pH was 2.7 (Cu^{2+}) and 5.5 (Zn^{2+}) on (B). The broken line, of which the slope is 2, was obtained by the least squares fitting. ●, Cu^{2+}; ○, Zn^{2+}.

in extraction, whereas the existence of *two* substituents on *each ortho*-position can be a origin of lowering extraction performance by steric hindrance.

Experimental

Apparatus

A Hitachi Model Z-6100 polarized Zeeman atomic absorption spectrophotometer was used for the determination of the concentration of a metal in aqueous solution. A Horiba Model F-12 pH meter equipped with a Horiba 9610-10D combined glass electrode was used to determine the pH values.

Reagents

The synthesis of H(p-Me)bsq was performed from 8-aminoquinoline and *p*-toluenesulfonyl chloride according to the reported procedure.[11]   Other 8-benzenesulfonamidoquinoline derivatives were prepared in a similar manner to H(p-Me)bsq from 8-aminoquinoline and the respective substituted benzenesulfonyl chlorides. The structures were identified by ^{1}H-NMR spectra and elemental analysis.

All other chemicals were reagent-grade materials and distilled deionized water was used throughout.

Distribution of the metals

The distribution of metal ions was studied as follows: In a centrifuge tube, an aliquot of chloroform (5 cm^3) containing 1×10^{-3} mol dm^{-3} of a ligand and equal volume of an aqueous phase containing 1×10^{-5} – 1×10^{-4} mol dm^{-3} of M^{2+} (M = Mn, Co, Ni, Cu, Zn, Cd or Pb), 1×10^{-1} mol dm^{-3} of potassium nitrate and 1×10^{-2} mol dm^{-3} of the buffer [chloroacetic acid, acetic acid, 2-morpholinoethanesulfonic acid (MES), 3-morpholino-propanesulfonic acid (MOPS) and *N*-tris(hydroxymethyl) methyl-3-aminopropanesulfonic acid (TAPS)] having no influence on the extraction, were shaken at 25±1°C for 2 – 4 h

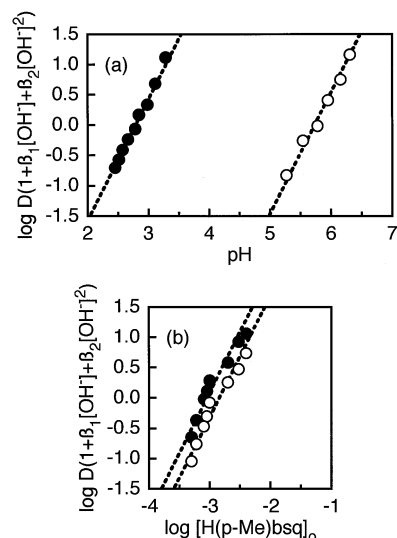(All of the extractions were equilibrated within 1 h, except the one for Ni^{2+} was within 3 h).   After the two phases were separated by centrifugation, the pH and the metal concentration in the aqueous phase were determined and the measured pH was used as the equilibrated pH. The metal concentration in the organic phase was determined after back-extraction into 1 mol dm^{-3} nitric acid.

Results and Discussion

General extraction selectivity

The extracted ratios (%E) of some divalent metals into chloroform with Hbsq, H(p-Me)bsq and H(2,4,6-Me$_3$)bsq were plotted as a function of the aqueous phase pH equilibrated with the organic phase in Fig. 2 as examples. All the studied ligands showed similar extraction selectivity for the divalent metal cations except Pb^{2+} as follows: Cu$^{2+} \gg$ Zn^{2+} > Cd$^{2+} \approx$ Co^{2+}> Ni^{2+} $\gg$ Mn^{2+}. The relatively high extractability for Zn^{2+} and the low one for Ni^{2+} seem to be common to ligands having sulfonamide-N-donor(s) as reported previously.[12]   In addition, relatively low extraction velocity for Ni^{2+} agreed with a previous report using H(p-Me)bsq and H(2,4,6-Me$_3$)bsq in chlorobenzene.[8]

The extraction equilibrium for M^{2+} on using the sulfonamide-type ligands may be assumed to follow this reaction:

$$M^{2+} + 2HL_o \rightleftharpoons ML_{2o} + 2H^+ \tag{1}$$

where subscript o denotes the species in the organic (chloroform) phase and HL denotes a ligand. In this case, the extraction constant (K_{ex}) can be expressed as follows:

$$K_{ex} = [ML_2]_o[H^+]^2/[M^{2+}][HL]_o^2 \tag{2}$$

In this case, the distribution ratio (D) of M^{2+} can be expressed as follows:

Table 1   Log K_{ex} values determined for divalent metal cations (25±1°C)

Cation	Hbsq	H(p-Me)bsq	H(2,4,6-Me$_3$)bsq	H(p-t-Bu)bsq	H(p-Cl)bsq
Mn^{2+}	N.D.[a]	N.D.[a]	N.D.[a]	N.D.[a]	N.D.[a]
Co^{2+}	−8.21±0.08	−7.93±0.13	−10.30±0.10	−8.62±0.05	−8.35±0.12
Ni^{2+}	−10.77±0.12	−10.39±0.36	N.D.[a]	N.D.[a]	−9.14±0.29
Cu^{2+}	0.97±0.03	0.44±0.04	−0.97±0.04	0.35±0.06	0.57±0.08
Zn^{2+}	−5.73±0.07	−5.54±0.04	−7.90±0.11	−5.88±0.13	−5.37±0.09
Cd^{2+}	−8.28±0.03	−8.42±0.02	−10.73±0.02	−8.62±0.01	−7.93±0.12
Pb^{2+}	−6.75±0.10	−7.34±0.04	N.D.[a]	−7.38±0.04	−7.01±0.03

Cation	H(o-NO$_2$)bsq	H(m-NO$_2$)bsq	H(p-NO$_2$)bsq	H(2,4-(NO$_2$)$_2$)bsq
Mn^{2+}	−12.52±0.03	−11.92±0.07	−12.12±0.03	−11.57±0.07
Co^{2+}	−7.42±0.03	−7.00±0.10	−7.04±0.06	−6.56±0.09
Ni^{2+}	−7.28±0.12	−8.41±0.04	−8.18±0.13	−7.50±0.17
Cu^{2+}	0.88±0.05	−1.66±0.06	1.56±0.05	2.12±0.02
Zn^{2+}	−4.96±0.02	−4.28±0.04	−5.36±0.05	−4.14±0.05
Cd^{2+}	−7.38±0.04	−7.02±0.03	−7.22±0.05	−6.41±0.05
Pb^{2+}	−6.03±0.05	−6.12±0.04	−6.37±0.04	−5.06±0.04

a. Not determined because of low extractability.

$$
\begin{aligned}
D &= [ML_2]_o/([M^{2+}] + [M(OH)^+] + [M(OH)_2]) \\
&= ([ML_2]_o/[M^{2+}]) \, (1 + \beta_1[OH^-] + \beta_2[OH^-]^2)^{-1} \\
&= (K_{ex}[HL]_o^2/[H^+]^2) \, (1 + \beta_1[OH^-] + \beta_2[OH^-]^2)^{-1} \qquad (3)
\end{aligned}
$$

where β_1 and β_2 are stability constants for hydroxo complexes of M(OH)$^+$ and M(OH)$_2$, respectively. From Eq. (3), validity of Eq. (1) can be confirmed by plotting log $D(1 + \beta_1[OH^-] + \beta_2[OH^-]^2)$ vs. pH at fixed [HL]$_o$ and plotting log $D(1 + \beta_1[OH^-] + \beta_2[OH^-]^2)$ vs. log[HL]$_o$ at fixed pH (The following β_i values for Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} were used for the calculation in this section: log β_1 = 3.40 4.35, 4.14, 6.30, 5.04, 3.92 and 6.29, and log β_2 = 5.80, 9.19, 9.00, 10.70, 11.09, 7.64 and 10.87, respectively).[13] Figure 3 shows these plots for Cu^{2+} and Zn^{2+} on H(p-Me)bsq system as examples. In all cases, the slope was close to 2 and the extraction equilibrium was found as shown in Eq. (1). In other words, it was found that Hbsq and its analogues do not form ML$_2$(HL)$_n$ species such as Hox. This seems to be due to the bulkiness of the (substituted) benzenesulfonyl group.

The log K_{ex} values calculated from experimental data using Eq. (3) are shown in Table 1. In this calculation, distribution of HL into aqueous phase was negligible because of its high hydrophobicity.

"Substituent on benzenesulfonyl group" effect

As shown in Table 1, introduction of *para*-alkyl substituent onto the benzenesulfonyl group in Hbsq (ex. H(p-Me)bsq and H(p-t-Bu)bsq) lead to hardly any enhancement in extractability or drastical change of extraction selectivity. This result seems to originate from the bulkiness of the benzenesulfonyl group itself. Namely, these substituents contribute little enhancement of the hydrophobicity of the ligands and, therefore, do not improve the stabilization of the extracted species.

Introduction of electron-withdrawing substituent such as –Cl and –NO$_2$, on the contrary, lead to enhancement in extractability. The effect of the latter was larger than that of the former. Furthermore, H(2,4-(NO$_2$)$_2$)bsq showed higher extraction performance than H(o-NO$_2$)bsq and H(p-NO$_2$)bsq, which qualitatively proves that this nature has additive property. These facts suggest that the substituent inductively enhances the acidity of >NH and thus prompts complexation between the dissociated >N$^-$ and metal cations.
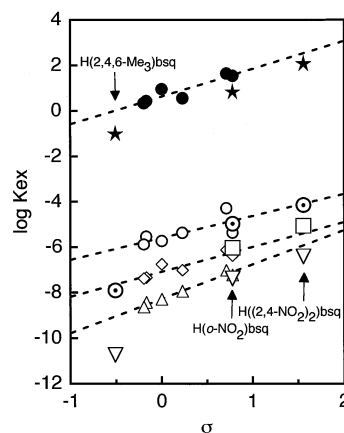

Fig. 4   Plots of the determined log K_{ex} vs. Hammett σ values. ●★, Cu^{2+}; ○⊙, Zn^{2+}; △▽, Cd^{2+}; ◇□, Pb^{2+}. The broken line was obtained by the least squares fitting using data on Hbsq, H(p-Me)bsq, H(p-t-Bu)bsq, H(p-Cl)bsq, H(m-NO$_2$)bsq and H(p-NO$_2$)bsq (These data were plotted using smaller ● ○ △ ◇ symbols). On plotting data on H(2,4,6-Me$_3$)bsq, H(o-NO$_2$)bsq and H(2,4-(NO$_2$)$_2$)bsq, the values of $3\sigma_{p\text{-Me}}$, $\sigma_{p\text{-NO}_2}$ and $2\sigma_{p\text{-NO}_2}$, respectively, were used as σ (These data were plotted using larger ★ ⊙ ▽ □ symbols).

It is interesting that the effect of o-NO$_2$ substituent was similar to that of p-NO$_2$, showing that of *a* bulky substituent on *an* *ortho*-position of the benzenesulfonyl group results in no steric hindrance on complexation. Possibly, the steric risk is avoided by rotating the benzene ring to the position that the substituent is directed near S=O bonds in >SO$_2$ group. To the contrary, lower extractability on the use of H(2,4,6-Me$_3$)bsq suggests that the existence of *two* substituents on *each ortho*-position of the benzenesulfonyl group brings on the steric hindrance, which cannot be avoided by the rotation. Namely, the one substituent seems to be not only directed near >N$^-$ coordination site but also pushed forward to the site because of steric repulsion between the another substituent and >SO$_2$ group.

To evaluate the discussion mentioned above numerically, log K_{ex} vs. Hammett σ[14] plots were produced. Figure 4 shows the plots for Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} as examples. The data on six extractants, Hbsq, H(p-Me)bsq, H(p-t-Bu)bsq, H(p-Cl)bsq,

H(m-NO$_2$)bsq and H(p-NO$_2$)bsq, were used for the determination of regression lines. The determined lines showed similar slopes (0.97 – 1.51, except for Ni^{2+} (2.59)) and relatively high correlation coefficients (0.843 – 0.972, except for Co^{2+} (0.770) and Zn^{2+} (0.542)), demonstrating the inductive effect. Furthermore, the data on H(o-NO$_2$)bsq (using $\sigma_{p\text{-NO}_2}$ as σ) and on H(2,4-(NO$_2$)$_2$)bsq (using $2\sigma_{p\text{-NO}_2}$ as σ) were placed close to the regression lines, whereas those on H(2,4,6-Me$_3$)bsq (using $3\sigma_{p\text{-Me}}$ as σ) were placed far from them. This fact supports the above-mentioned discussion concerning steric effect.

As conclusive words, we points out that the "substituent on benzenesulfonyl group" effect studied here is obviously not peculiar to Hbsq but will be common to any ligands having benzenesulfonamide group. That is to say, the inductive effect and the steric effect mentioned above can be a factor to control extraction performance of all of the benzenesulfonamide-type ligands.

Acknowledgements

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