Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A Molecular Modeling Study of Zinc(II) Extraction by Substituted 8-Hydroxyquinolines in the Presence of Various Pyridinic Adducts

C. Sella[a]; D. Bauer[a]
[a] Laboratoire De Chimie Analytique, E.S.P.C.I., Paris, France

To cite this Article Sella, C. and Bauer, D.(1993) 'A Molecular Modeling Study of Zinc(II) Extraction by Substituted 8-Hydroxyquinolines in the Presence of Various Pyridinic Adducts', Separation Science and Technology, 28: 13, 2137 — 2148

To link to this Article: DOI: 10.1080/01496399308016739

URL: http://dx.doi.org/10.1080/01496399308016739

SEPARATION SCIENCE AND TECHNOLOGY, **28**(13&14), pp. 2137–2148, 1993

A Molecular Modeling Study of Zinc(II) Extraction by Substituted 8-Hydroxyquinolines in the Presence of Various Pyridinic Adducts*

C. SELLA and D. BAUER
LABORATOIRE DE CHIMIE ANALYTIQUE
E.S.P.C.I.
10, RUE VAUQUELIN, 75005 PARIS, FRANCE

ABSTRACT

Molecular modeling is used to account for the extraction of zinc(II) by 8-hydroxyquinoline and 2-methyl and 4-methyl analogues in chloroform in the presence of pyridine and its 2-methyl, 4-methyl, and 2,4,6-trimethyl derivatives. The species of formula ZnQ_2B and $ZnQ_2B(H_2O)$ are modeled, where Q^- is an 8-hydroxyquinolinate anion and B is the 8-hydroxyquinoline itself or a pyridinic adduct. Each complex has an energy value which characterizes its steric and electrostatic parts and which allows comparison among complexes. This study accounts for the steric hindrances produced by methyl groups in the 2- and 6-positions of the pyridine ring and those produced by the methyl group in the 2-position of the 8-hydroxyquinolinate anion. It also accounts for the improvement of the stability of complexes when the 8-hydroxyquinolinate anion has a methyl group in the 4-position. The energy of the modeled pyridinic adduct complexes decreases when the extraction constant is increased, as has been observed for other species in previous work.

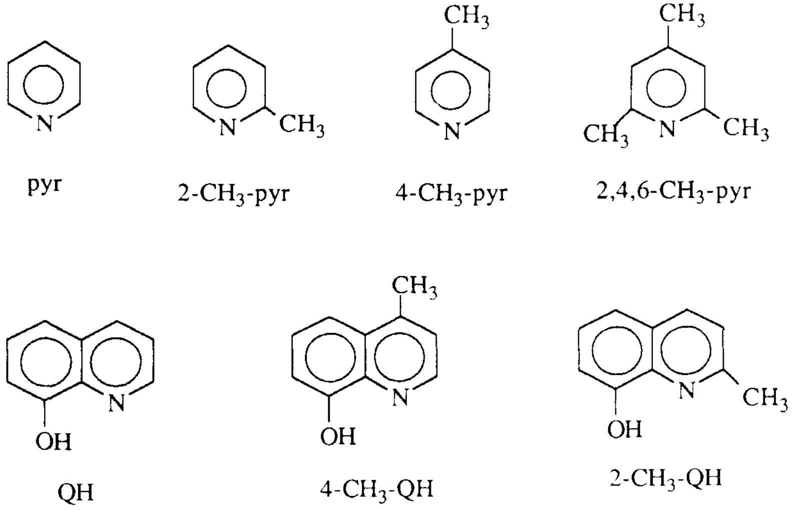
INTRODUCTION

Molecular modeling is a means of visualizing extractable species, extractants, and extracted complexes, but it can also help to calculate the atomic charge distribution and to quantify the steric and electrostatic effects of these species by the energy minimization procedure. This quantification allows us to compare the modeled complexes and to consider structure–activity relationships based on the assumption that correlations exist

---

* This paper is dedicated to Professor W. Nitsch, who has made many impressive contributions in the area of solvent extraction over the years, on the occasion of his 60th birthday.

between the energy of modeled complexes and the stability of extracted complexes or the ability to be extracted. The experimental extraction percentage or the stability constant of complexes quantify this ability. The molecular modeling software used is SYBYL, developed by Tripos Associates (1). Previous studies (2–4) have shown that molecular modeling can be used to account for the results of solvent extraction of dianions by dianion-exchange extractants such as diphosphonium compounds. The modeled complexes were ion-pair species. In the present work we investigated the differences of extractibilities of zinc 8-hydroxyquinolinate adduct complexes. Zinc(II) is extracted as the complex $ZnQ_2B(H_2O)_a$ (with $a = 0$ or 1), where Q^- is 8-hydroxyquinolinate anion and B is the 8-hydroxyquinoline HQ itself (self-adduct) or a pyridinic molecule. We considered three 8-hydroxyquinolinate anions (8-hydroxyquinolinate, 2-methyl-8-hydroxyquinolinate, 4-methyl-8-hydroxyquinolinate) and four pyridinic adducts (pyridine, 2-methylpyridine, 4-methylpyridine, 2,4,6-trimethylpyridine). The structures of these ligands are presented in Fig. 1. This example is taken from literature (5, 6) in which data about adduct formation constants (K_{AD}), determined in chloroform, are reported. There is a competition between the steric effect produced by the methyl groups and the synergistic effect produced by the increase in basicity due to the methyl groups. The adduct formation constant is the resultant of these two effects. So, in this work the modeled complexes are metal complexes.



pyr 2-CH3-pyr 4-CH3-pyr 2,4,6-CH3-pyr

QH 4-CH3-QH 2-CH3-QH

FIG. 1 Structure of pyridinic adducts and substituted 8-hydroxyquinoline compounds.

The molecular mechanics force field implemented in the SYBYL software produces molecular geometries of organic molecules (7). Unfortunately, there is a shortcoming in this force field in accounting for metal—ligand bonds. The development of an accurate force field for the inorganic system is difficult because of the relative weak nature of M—L and M—M bondings and the considerable influence of electronic effects on these bondings (8). Nevertheless, we have the possibility of introducing into the software the parameters of metal atoms and their bonding characteristics. In this work we have developed an approximative force field for the Zn—O and Zn—N bonds present in zinc-8-hydroxyquinolinate adduct complexes.

COMPUTATIONAL METHODS

In the laboratory, the SYBYL molecular modeling package (version 5.41) runs on a VAX3200/VMS workstation and operates on the PS300 terminal with the NITRO graphics interface. To model a metal complex, we introduce in the software the parameters necessary for defining the molecular mechanics force field of the metal—ligand bonds involved in the complex. We follow a procedure similar to the one developed and used in previous work (3, 9). The parameters required to define zinc(II) are given in Table 1.

X-ray diffraction studies (10) have been made on a series of compounds of the type $MQ_2(H_2O)_2$ where M is such metal ions as Zn^{2+} and Q^- is 8-hydroxyquinolinate anion. The results of these investigations show that two chelating 8-hydroxyquinolinate anions coordinate to the metal by forming a *trans*-planar structure and that two water molecules occupy the axial positions to complete a six-coordinate structure. There is a sort of distorted octahedral arrangement of bonds around the central zinc ion. It is suggested from a study of the infrared absorption spectra of cobalt(II) and nickel(II)-8-hydroxyquinolinate that the adduct complexes with a pentacoordination have a square pyramidal structure (11). So, we introduced the Zn^{2+} metal ion with its octahedral geometry. Complexes of formula

TABLE 1
Parameters Required to Define Zn(II)

Heteroatom symbol:	Zn	Formal charge on the atom:	2
Valency:	6	Number of lone pairs:	0
Geometry:	Octahedral	Atomic weight:	65.38 g·mol^{-1}
Electronegativity:	1.65 (12)	Hydrogen bond acceptor:	No
Atomic number:	30	Hydrogen bond donor:	No
Van der Waals radius:	1.4 Å (13)		

$ZnQ_2B(H_2O)$, which have a hexacoordination, are modeled with 8-hydroxyquinolinate anions in the *trans*-equatorial positions and with B and H_2O in the axial positions. Complexes of formula ZnQ_2B, which have a pentacoordination, are modeled with 8-hydroxyquinolinate anions in the *trans*-equatorial positions and with B in one of the axial positions. The bonds are defined by the geometrical parameters (bond type, bond length, bond angle) and the corresponding force-field constants. The values of the geometrical parameters are obtained from x-ray results (10), and the values of the force-field constants are estimated or calculated from low frequency infrared spectra data (14) as in previous work (3, 9). The geometrical parameters and force-field constants added in our own database are given in Table 2. The force field being defined, the complexes are modeled and minimized by taking into account their atomic charge distribution calculated by a semiempirical molecular orbital method (Mopac). The energy minimization procedure (Maximin2) consists of moving the atoms of a molecule in such a way as to always reduce the total energy of the system based on an empirical representation of the interaction energy of the molecule [by means of several potential functions (bending, stretching, torsional, van der Waals, electrostatic, their cross terms) and their experimentally derived parameters].

The value of the total minimized energy E_t is only a measure of intramolecular strain relative to a hypothetical situation. The energy E_t can be divided into two terms, one corresponding to a steric energy (E_s) and the

TABLE 2

Geometric Parameters and Force-Field Constants (lengths in Å, angle in degrees, σ in cm^{-1}, $k_{stretching}$ in $kcal \cdot mol^{-1} \cdot Å^{-2}$, $k_{bending}$ and $k_{twisting}$ in $kcal \cdot mol^{-1} \cdot degree^{-2}$, * represents any atom name). O_w is the Oxygen in H_2O

Bond length	Atom1	Atom2	Type	Length (10)	$k_{stretching}$	σ (14)
	Zn	N	1	2.06	43	210
	Zn	O	1	2.05	76	264
	Zn	O_w	1	2.27	46	205

Bond angle	Atom1	Atom2	Atom3	Angle	$k_{bending}$
	*	Zn	*	90	0.04
	H	O_w	Zn	125	0.02

Bond torsion	Atom1	Atom2	Atom3	Atom4	Type	$k_{twisting}$	Periodicity
	*	Zn	N	*	1	0.2	4
	*	Zn	O	*	1	0.2	4

other corresponding to an electrostatic energy (E_e). By itself, E_t, being an absolute energy, has no physical meaning. The most stable conformations (with the lowest value of minimized energy) are obtained from systematic conformational searches which systematically explore the different viable conformations. The comparison of the complexes' energy is not obvious when they have atoms different in number and in nature. In this case we compare the association energy calculated as follows: the sum of the total energies of separated species involved in a complex is subtracted from the total energy of the complex.

$$E_{\text{ass}} = E_{\text{t complex}} - \sum_{\text{ligand}} E_{\text{t ligand}}$$

In this paper we try to check if the complex with the smallest energy value corresponds to the most stable extractable complex. The association energy is a parameter which allows us to compare the modeled complexes and to correlate them with their extraction constant (K_{ex}).

RESULTS AND DISCUSSION

The role of adduct formation in the extraction of zinc with 8-hydroxyquinoline has been studied in previous work (5, 6, 14–17). Zinc-8-hydroxyquinolinate, precipitated from aqueous solution, is not soluble in chloroform due to the formation of such hydrated forms as $ZnQ_2(H_2O)_2$; the oven-dried precipitate, however, is soluble (10, 15). From the distribution data, Stary (16) concluded that zinc(II) is extracted by 8-hydroxyquinoline in chloroform as the complex $ZnQ_2(HQ)_2$. Schweitzer et al. (17) investigated the extraction of zinc-8-hydroxyquinolinate into 10 different organic solvents S: the species extracted with 4-methyl-2-pentanone, 1-butanol, and 4-methyl-2-pentanol is ZnQ_2S_2; that extracted with benzene and chloroform is $ZnQ_2(HQ)S$; that extracted with butyl and pentyl ethers is ZnQ_2S; that extracted with carbon tetrachloride is $ZnQ_2(HQ)$; and that extracted with hexane and cyclohexane is $ZnQ_2(H_2O)_2$. It is suggested that the extraction behavior can be explained by assuming that a water molecule is attached to the ZnQ_2S and $ZnQ_2(HQ)$ species. Chou et al. (5, 6) studied the extraction of zinc with substituted 8-hydroxyquinoline. Zn(II) was found to be extracted with chloroform containing 8-hydroxyquinoline and the 4-methyl analogue as $ZnQ_2(HQ)$. In the case of the 2-methyl analogue, the extractable complex is the simple chelate ZnQ_2. The reason for this difference probably results from the steric hindrance to adduct formation presented by the substituent in the 2-position. Pyridine and its 2-methyl, 4-methyl, and 2,4,6-trimethyl derivatives have been found to enhance the extraction of Zn(II) in chloroform with either 8-

hydroxyquinoline or its 2-methyl and 4-methyl analogues. In the formation of self-adduct or pyridine adduct complexes, it was assumed that one of the water molecules was replaced by the 8-hydroxyquinoline or pyridine molecule and the other remained attached, whereas in the extraction of an adduct of 2-methyl or 2,4,6-trimethylpyridine, when 1 molecule of water was replaced by these ligands, the other water molecule was pushed out of the coordination sphere by the sterically hindering methyl groups.

In the present work we investigated the example developed by Chou et al. (5, 6). The extraction reaction can be written as

$$Zn^{2+} + 2\overline{HQ} + \overline{B} + aH_2O \rightarrow \overline{ZnQ_2B(H_2O)_a} + 2H^+, \qquad \text{with } a = 0 \text{ or } 1$$

The bar notation indicates a species in an organic phase, and the absence of a bar implies the species is in an aqueous phase.

The overall formation constants of the zinc chelates in water, as well as the adduct formation constants in the organic phase, have been evaluated in Refs. 5 and 6 from such experimental data as the equilibrium distribution ratios and by considering the adduct complex ZnQ_2B; the water activity is not involved in the equilibrium constants. The extraction constant of the adduct complex, K_{ex}, is defined as

$$K_{ex} = \frac{(\overline{ZnQ_2B})(H^+)^2}{(Zn^{2+})(\overline{HQ})^2(\overline{B})}$$

K_{ex} can be express as a function of other constants whose values are reported in the literature (6, 18).

$$K_{ex} = K_{AD}K, \qquad \text{with } K = \frac{K_{DC}K_f k_a^2}{K_{DR}^2}$$

where K_{AD} is the adduct formation constant, K_{DC} is the distribution coefficient of the chelate ZnQ_2, K_f is the overall formation constant of ZnQ_2 in the aqueous phase, k_a is the acidic constant of HQ, and K_{DR} is the distribution coefficient of HQ.

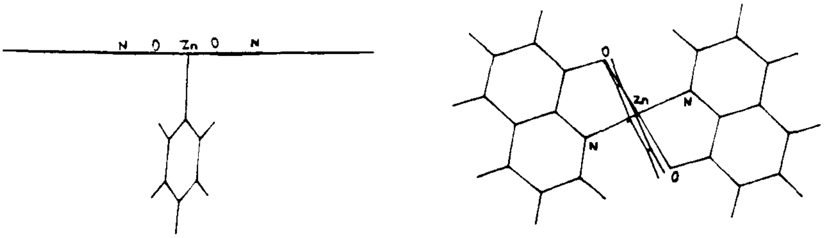
K is dependent on 8-hydroxyquinoline and K_{AD} is dependent on 8-hydroquinoline and the adduct. The values of K_{ex}, K, and K_{AD} (6) are reported in Table 3.

The complexes of formulas ZnQ_2B and $ZnQ_2B(H_2O)$ are modeled with three 8-hydroxyquinolines and five adducts even if they are probably not extracted; e.g., zinc-2-methyl-8-hydroxyquinolinate self-adduct complex or the complexes of formula $ZnQ_2B(H_2O)$, where the 8-hydroxyquinolinate anion is $2\text{-}CH_3\text{-}Q^-$ or Q^- or $4\text{-}CH_3\text{-}Q^-$ and the adduct is $2\text{-}CH_3$-pyr or $2,4,6\text{-}CH_3$-pyr.

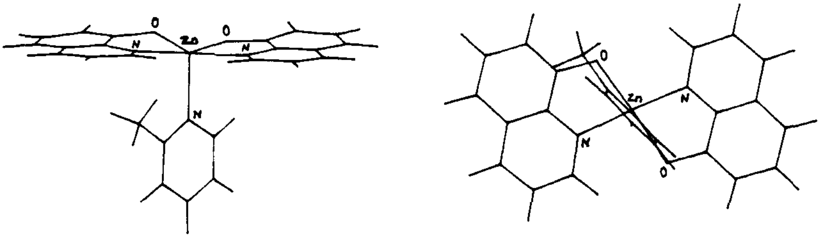
The modeled complexes ZnQ_2pyr and $ZnQ_2(2\text{-}CH_3\text{-pyr})$ are presented in Fig. 2 from two points of view, above and on one side of the chelating

TABLE 3
Values of K_{ex}, K, and K_{AD} (6)

Adduct	4-CH_3-pyr	pyr	2-CH_3-pyr	2,4,6-CH_3-pyr	Self-adduct
4-CH_3-Q:					
log K_{AD}	2.87	2.47	2.00	1.50	2.20
(log K = −6.86) log K_{ex}	−3.99	−4.39	−4.86	−5.36	−4.66
Q:					
log K_{AD}	3.40	3.05	2.10	1.50	2.17
(log K = −7.76) log K_{ex}	−4.36	−4.71	−5.66	−6.26	−5.59
2-CH_3-Q:					
log K_{AD}	1.75	1.60	1.00	0.20	—
(log K = −7.91) log K_{ex}	−6.16	−6.31	−6.91	−7.71	—



ZnQ2pyr



ZnQ2(2-CH3-pyr)

FIG. 2 Modeled complexes ZnQ_2pyr and $ZnQ_2(2\text{-}CH_3\text{-}pyr)$ represented from two points of view, above and on one side of the chelating plane.

plane. The complexes are simply represented by lines corresponding to the bonds between atoms. This figure shows that the steric hindrance caused by the methyl group on the 2- or 6-position of the pyridine ring interferes with the chelating plane. For the complex ZnQ_2pyr, we can show the complex in a side view where the metal ion and two 8-hydroxyquinolinate anions are placed in the equatorial plane (the plane is seen as a line). For the complex $ZnQ_2(2\text{-}CH_3\text{-}pyr)$, it is impossible to see the same thing because the metal ion and the two 8-hydroxyquinolinate anions are not placed in a plane. In this case the chelating plane is distorted by the methyl group in the 2-position of the pyridine ring. Thus, it is easy to imagine from these observations that the water molecule can be pushed out of the coordination sphere by the sterically hindering methyl groups when the chelating plane is distorted.

Each complex is characterized by an association energy, the values of which are reported in Figs. 3a and 3b. The pyridinic adducts are placed on the abcissas, following an increasing log K_{AD} or log K_{ex} order. The energy values of modeled complexes which are probably not extracted are encircled. The very unstable complexes which exist only in the presence of an excess amount of pyridine are surrounded by a dashed ring. The enclosed values are located above 17 kcal·mol^{-1} and the most stable complexes are below that value. This is in agreement with our assumption that the complexes with the smallest energy values correspond to the most stable complexes.

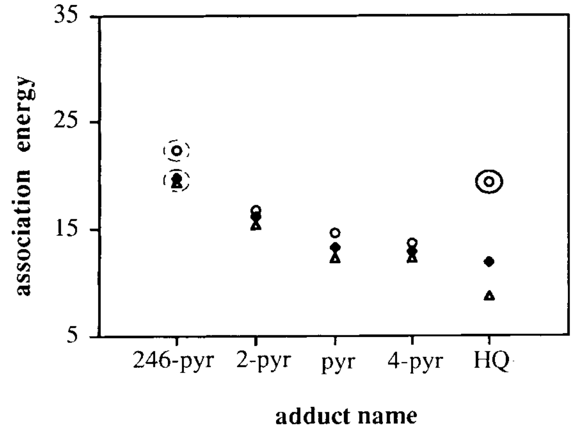


FIG. 3a Association energy (kcal·mol^{-1}) of modeled complexes of formula ZnQ_2B versus B for three 8-hydroxyquinolinate anions: (○) $2\text{-}CH_3\text{-}Q^-$; (◆) Q^-; (△) $4\text{-}CH_3\text{-}Q^-$.

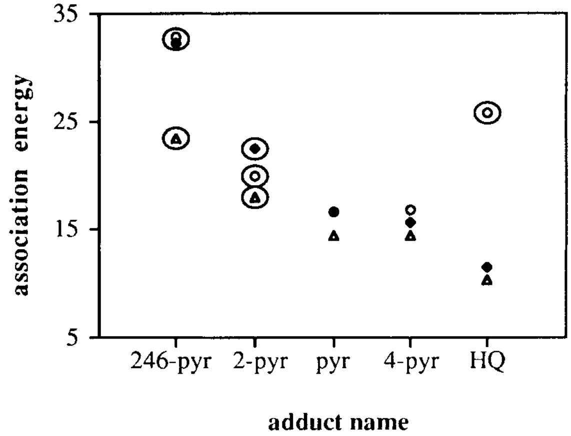


FIG. 3b Association energy (kcal·mol^{-1}) of modeled complexes of formula $ZnQ_2B(H_2O)$ versus B for three 8-hydroxyquinolinate anions: (○) 2-CH_3-Q^-; (◆) Q^-; (△) 4-CH_3-Q^-.

Comparison of the energy values of complexes of formulas ZnQ_2B and $ZnQ_2B(H_2O)$, where the adduct is 2-CH_3-pyr or 2,4,6-CH_3-pyr, and the 8-hydroxyquinolinate anion is 2-CH_3-Q^-, Q^-, or 4-CH_3-Q^-, shows that the complexes without water molecule have the lowest energy values and should be the most stable. The differences of energy between the complexes of formulas ZnQ_2B and $ZnQ_2B(H_2O)$ (without and with a water molecule) are low when the adduct is pyr or 4-CH_3-pyr and the 8-hydroxyquinolinate anion is 2-CH_3-Q^-, Q^-, or 4-CH_3-Q^-. In these cases the possibilities of the formation of complexes with a water molecule are not to be excluded even though the energies of complexes of formula $ZnQ_2B(H_2O)$ are slightly higher than those of complexes of formula ZnQ_2B. For a given 8-hydroxyquinoline, the complexes modeled with pyridine and 4-methylpyridine show similar energy values.

Therefore, the molecular modeling study of pyridinic adduct complexes illustrates the steric hindrances produced by methyl groups in the 2- and 6-positions of the pyridine ring but does not account clearly for the synergistic effect produced by the increase in basicity due to the methyl group in the 4-position of the pyridine ring.

Figure 4 shows the variations of the association energy of pyridinic adduct complexes versus log K_{ex} for each 8-hydroxyquinoline, considering the complexes of formula ZnQ_2B and $ZnQ_2B(H_2O)$. According to our assumption, the energy values decrease when log K_{ex} is increased.

In most cases the energy values of complexes modeled with a given B adduct and different 8-hydroxyquinolinate anions are in the following order: 4-CH_3-Q $<$ Q^- $<$ 2-CH_3-Q^-. The log K_{ex} values are in the opposite

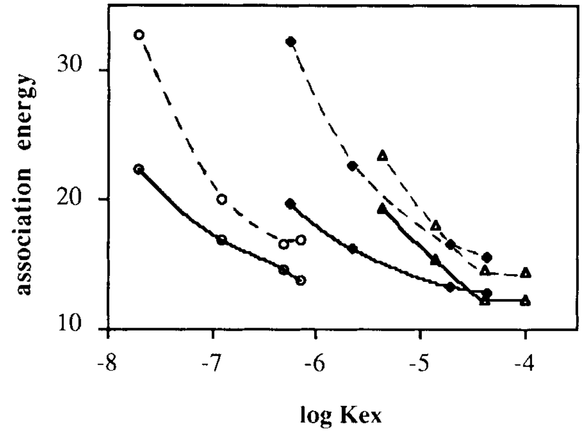


FIG. 4 Association energy (kcal·mol^{-1}) of modeled pyridinic adducts of formula ZnQ_2B (——) and $ZnQ_2B(H_2O)$ (- -) versus log K_{ex} for three 8-hydroxyquinolinate anions: (○) 2-CH_3-Q^-; (◆) Q^-; (△) 4-CH_3-Q^-.

order. For a given adduct B, the study accounts for the improvement of the stability of complexes when the 8-hydroxyquinolinate anion has a methyl group in the 4-position and for the steric hindrance introduced by a methyl group in the 2-position of the 8-hydroxyquinolinate anion.

The modeled zinc-8-hydroxyquinolinate self-adduct complex of formula $ZnQ_2(HQ)$ is presented in Fig. 5. The chelating plane has a slight distortion

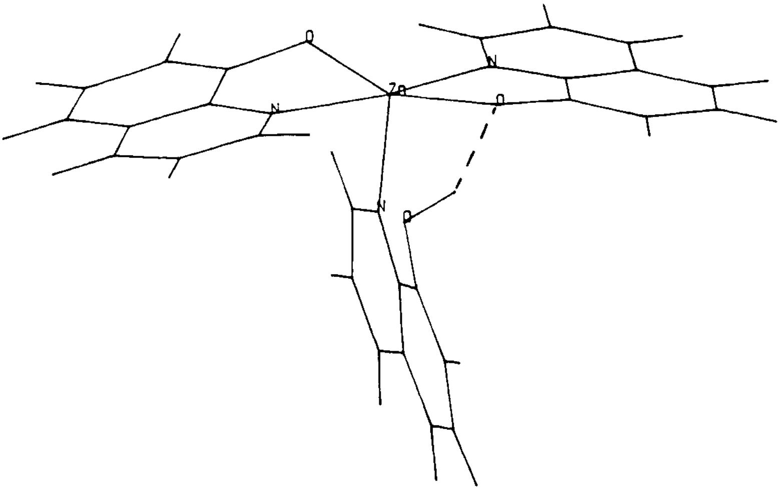


FIG. 5 Modeled self-adduct $ZnQ_2(HQ)$.

but the structure is stabilized by the presence of hydrogen bonding between the hydrogen of the hydroxyl group of 8-hydroxyquinoline and the oxygen of one 8-hydroxyquinolinate anion. The hydrogen bonding is represented by a broken line. The self-adducts of zinc-8-hydroxyquinolinate and zinc-4-methyl-8-hydroxyquinolinate have lower energies than the pyridinic adducts (Figs. 3a and 3b) because of the hydrogen bonding.

When the 8-hydroxyquinoline has a methyl group in position 2, the hydrogen bonding still exists but the chelating plane has a high distortion. The increase in steric hindrance involves higher energy values of the modeled complexes (Figs. 3a and 3b). This is the reason why the self-adduct of zinc-2-methyl-8-hydroxyquinolinate is not extracted.

CONCLUSION

The extraction of zinc with different 8-hydroxyquinolines in the presence of pyridinic adducts involves the formation of adduct complexes of formula ZnQ_2B and $ZnQ_2B(H_2O)$ in the organic phase. These complexes are modeled and characterized by energy values which quantify the steric and electrostatic effects. A molecular modeling study of pyridinic adducts allows us to account for the steric hindrances produced by methyl groups in the 2- and 6-positions of the pyridine ring and those produced by the methyl group in the 2-position of the 8-hydroxyquinolinate anion. This study also accounts for the improvement of the stability of complexes when the 8-hydroxyquinolinate anion has a methyl group in the 4-position. The energy of the modeled pyridinic adducts decreases when log K_{ex} is increased.

REFERENCES

1. Tripos Associates Inc., 1699 S. Hanley Road, Suite 303, St. Louis, Missouri 63144, SYBYL 5.41 (988).
2. C. Sella and D. Bauer, *Solv. Extr. Ion Exch.*, *10*, 491 (1992).
3. C. Sella and D. Bauer, *Ibid.*, *10*, 579 (1992).
4. C. Sella and D. Bauer, To Be Published.
5. F. C. Chou, Q. Fernando, and H. Freiser, *Anal. Chem.*, *37*, 361 (1965).
6. F. C. Chou and H. Freiser, *Ibid.*, *40*, 35 (1968).
7. M. Clark, R. D. Cramer III, and N. Van Opdenbosch, *J. Comp. Chem.*, *10*, 982 (1989).
8. S. E. Saum, S. A. Laneman, and G. G. Stanley, *Inorg. Chem.*, *29*, 5065 (1990).
9. F. Fourcot, Thèse de Doctorat de l'Université Paris VI, 1991.
10. L. L. Merritt, J. Richard, T. Cady, and B. W. Mundy, *Acta Cryst.*, *7*, 473 (1954).
11. A. T. Rane and V. V. Ravi, *Spectrochim. Acta*, *38A*, 937 (1982).
12. A. L. Allred, *J. Inorg. Nucl. Chem.*, *17*, 215 (1961).
13. A. Bondi, *J. Phys. Chem.*, *68*, 441 (1964).
14. N. Ohkaku and K. Nakamoto, *Inorg. Chem.*, *10*, 798 (1971).

15. A. T. Rane, *J. Sci. Ind. Res.*, *43*, 261 (1984).
16. J. Stary, *Anal. Chim. Acta*, *28*, 132 (1963).
17. G. K. Schweitzer, R. B. Neel, and F. R. Clifford, *Ibid.*, *33*, 514 (1965).
18. J. Stary and H. Freiser, *Equilibrium Constants of Liquid–Liquid Distribution Reactions. Part IV—Chelating Extractants*, IUPAC, Pergamon Press, 1978.

Received by editor December 10, 1992