Solubilities of Chelating Ligands Dibenzoylmethane, 1,10-Phenanthroline, and 8-Hydroxyquinoline in Supercritical Carbon Dioxide

Mojtaba Shamsipur,*,† Ali Reza Ghiasvand,‡ and Yadollah Yamini‡

Departments of Chemistry, Razi University, Kermanshah, Iran, and Tarbiat Modarres University, Tehran, Iran

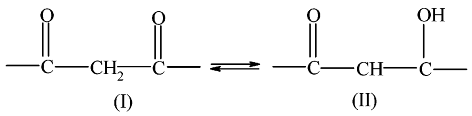
The equilibrium solubilities of dibenzoylmethane, 1,10-phenanthroline, and 8-hydroxyquinoline have been measured in supercritical carbon dioxide using a simple and reliable static method. Solubility isotherms were obtained at (308, 318, 328, 338, and 348) K in the pressure range (101 to 355) bar; solubilities increased linearly with increasing density at constant temperature and increased with increasing temperature at high densities. The solubilities obtained were correlated with the density of carbon dioxide by using Bartle's semiempirical equation. The calculated solubilities show good agreement with the experimental data.

Introduction

Recently, supercritical fluids (SFs) modified by the addition of suitable complexing agents have been utilized in the extraction of metal ions from various solid and liquid matrixes.[1−9] This has opened a whole area of research into the use of SFs as an environmentally acceptable technology, as an analytical preconcentration technique, and as an extractive system for large-scale metallurgical extraction.[10]

The first and most important requirement for the selection of suitable ligands for the supercritical extraction (SFE) of metal ions includes the study of solubility in SFs at acceptable ranges of temperature and pressure for the ligands that show good selectivity and high efficiency for the extraction of proper metal ions. Some researchers have worked on the solubility determination of various ligands and metal chelates in SF CO_2.[11−16]

An important class of chelating agents includes β-diketones, present in both keto (I) and enol (II) forms, as follows:



$$-\overset{\overset{O}{\parallel}}{C}-CH_2-\overset{\overset{O}{\parallel}}{C}- \rightleftharpoons -\overset{\overset{O}{\parallel}}{C}-CH-\overset{\overset{OH}{|}}{C}-$$

(I) (II)

In their reaction with metals, the β-diketones yield six-membered chelating rings. Aromatic derivatives yield more stable complexes then their aliphatic analogues. The most important β-diketones are acetylacetane (AA), thenoyltrifluoroacetone (TTA), and dibenzoylmethane (DBM). DBM has been used for the extraction and photometric determination of metal ions.[17−19]

8-Hydroxyquinoline (HOX) reacts with many metal ions to form stable chelate compounds that can be readily extracted in organic solvents. Although many cationic species yield HOX complexes of the $M(OX)_n$ type, with bivalent cations, it has been shown that complexes of type $M(OX)_n{\cdot}HOX$ and $M(OH)_n{\cdot}2HOX$ can be extracted into organic phases. HOX (1%) dissolved in $CHCl_3$ is usually used for the extraction, separation, and photometric determination of different metal ions.[19,20]

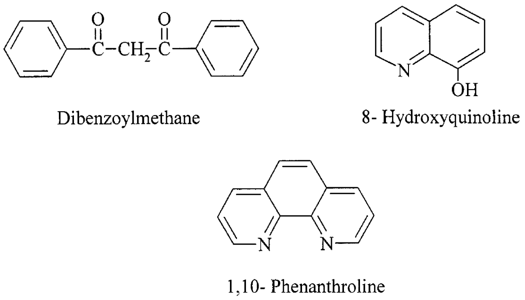


Figure 1. Structures of dibenzoylmethane (DBM), 8-hydroxyquinoline (HOX), and 1,10-phenanthroline (phen).

1,10-Phenanthroline (phen) reacts rapidly with Fe(II) ions over a wide range of pH to give an orange-red or pink complex.[19] Recently 1,10-phenonthroline was used for the extraction of Ag(I)[21] and trivalent lanthanide ions.[22]

The possibility of selecting chelating ligands DBM, HOX, and phen in chelation−SFE studies of metal ions obviously depends on the solubilities of these ligands and their metal ion complexes in pure or modified SF CO_2. In the present study, the solubilities of DBM, HOX, and phen (Figure 1) were measured in SF CO_2 over wide ranges of temperature and pressure. The measured solubilities were nicely correlated using a semiempirical model proposed by Bartle.[23,24]

Experimental Section

Materials. Carbon dioxide of 99.99% mass purity (Sabalan, Tehran, Iran) was used for all extractions. HPLC-grade methanol (Merck) was used as received. Reagent-grade dibenzoylmethane (DBM, Fluka), 8-hydroxyquinoline (HOX, Merck), and 1,10-phenanthroline (Phen, Merck) were of the highest purity available and were used as received.

Apparatus and Procedures. A Suprex MPS/225 integrated SFE−SFC system modified for solubility determination in SFE mode was used. A complete description of

---

* To whom correspondence should be addressed. E-mail: mshamsipur@yahoo.com.
† Razi University.
‡ Tarbiat Modarres University.

10.1021/je034098j CCC: $27.50

Table 1. Solubilities of Dibenzoylmethane (DBM), 8-Hydroxyquinoline (HOX), and 1,10-Phenanthroline (phen) in Supercritical Carbon Dioxide

			DBM		HOX		phen	
T/K	P/bar	ρ/kg·m^3	s/g·dm^{-3}	10^4x	s/g·dm^{-3}	$10^4\,x$	s/g·dm^{-3}	10^4x
308	101	712	2.7	7.3	5.50	23.2	0.3	1.0
	152	817	5.4	13.0	9.60	35.4	0.5	1.5
	203	868	5.7	12.8	12.1	42.1	0.6	1.6
	253	903	7.8	16.9	14.3	47.7	0.7	2.0
	304	931	8.4	17.6	16.3	52.7	0.9	2.4
	355	956	10.5	21.5	17.1	54.0	1.2	2.9
318	101	514	1.8	6.7	1.8	10.9	0.2	0.8
	152	747	4.0	10.5	10.7	43.3	0.4	1.4
	203	816	6.6	15.9	15.2	56.1	0.8	2.5
	253	860	9.6	21.9	18.2	63.9	1.1	3.1
	355	920	17.7	37.6	24.4	79.6	1.7	4.5
328	101	339	0.5	3.0	1.0	8.7	0.1	0.6
	152	658	2.7	8.2	10.8	49.5	0.4	1.4
	203	758	9.6	24.7	18.2	72.6	1.0	3.1
	253	814	15.7	37.7	24.4	90.0	1.4	4.2
	304	854	19.8	45.3	29.6	103.9	1.7	4.8
	355	886	27.4	60.3	34.3	116.0	2.1	5.9
338	101	273	0.1	1.0	1.3	14.0	0.03	0.3
	152	562	2.2	7.5	9.6	51.4	0.3	1.4
	203	695	11.3	31.8	19.2	83.1	1.2	4.3
	253	765	22.2	56.7	27.1	106.3	1.7	5.5
	304	814	32.0	76.5	39.3	144.2	2.2	6.6
	355	849	43.5	99.5	47.6	167.1	2.8	8.0
348	101	238					0.02	0.2
	152	477					0.3	1.5
	203	634					1.3	5.2
	253	717					2.2	7.3
	304	772					2.9	9.2
	355	812					3.5	10.4

this system was reported in one of our previous papers.[25] Solubility measurements were accomplished with a 1-mL extraction vessel in the pressure range (101 to 355) bar at temperatures (308, 318, 328, and 338) K for DBM and HOX and (308, 318, 328, 338, and 348) K for phen for a duration of 30 min. It should be noted that, by monitoring the solubility data versus time, 30 min was found to be adequate to ensure the attainment of equilibrium. The equilibrium temperatures and pressures were measured to accuracies of ±1 K and ±0.5 bar, respectively. The solid solutes (100 to 200) mg were mixed well with 1 g of glass beads and packed into the extraction vessel. This procedure prevents channeling, increases the contact surface between the sample and the SF, eliminates the dead volume and, consequently, reduces the equilibration time.

A 2100 Shimadzu UV−vis spectrophotometer was used for solubility determination by absorbance measurements at $\lambda_{\max}$ of each compound. Stock solutions of DBM, HOX, and phen (1000 μg·mL^{-1}) were prepared by dissolving appropriate amounts of the solid samples in methanol, and a set of the standard solutions were then prepared by the appropriate dilution of stock solutions. The calibration curves obtained (with regression coefficients better than 0.999) were used to establish the concentrations of DBM, HOX, and phen in the collection vial. The solubilities of the solutes were generally reproducible within ±3%.

Results and Discussion

The reliability of the apparatus was preliminarily checked by measuring the solubility of naphthalene in supercritical CO_2 at 308 K, as described before.[25] The experimental solubilities in mole fraction (x) of the solute and in grams per liter of the solute in supercritical CO_2 (s) are summarized in Table 1. Each reported solubility is the average of three replicate measurements.

From the data given in Table 1, it is readily seen that the solubility of ligands increases with increasing pressure at constant temperature. The effect of pressure on the solubility is more significant. This is in agreement with conventional wisdom, stating that the density of a SF must increase in order to increase the solubility and extraction efficiency.[26]

An examination of the temperature effect on the solubility data (Table 1) reveals the existence of retrograde (crossover) pressure effect behavior for all three ligands in supercritical CO_2. At pressures above the crossover region (about 150 bar), solubilities increase with both increasing pressure and temperature, but below this region, solubilities increase with increasing pressure but decrease with increasing temperature. The different effect of temperature on solubility could be due to influences of temperature on such diverse properties as the solute vapor pressure, the solvent density, and intermolecular interactions in the supercritical fluid phase. At lower pressures where the density effect is predominant, the fluid density is lowered by small increases in temperature. At higher pressures, the fluid density is less dependent on temperature so that the observed increase in solubility with temperature could be primarily due to other factors, especially the higher vapor pressure of the solid samples.

Predicting the equilibrium solubility of solutes in SF solvents is very important for SFE and SFC. To carry out an SFE experiment, it is necessary for the analyte to be sufficiently dissolved in the SF solvent. Thus, without knowledge of solubility phenomena, the optimization of SFE conditions can be done only by trial and error. The experimental solubility data for ligands were correlated using the equation proposed by Bartle,[23,24]

$$\ln\left(\frac{xP}{P_{\text{ref}}}\right) = A + C(\rho - \rho_{\text{ref}}) \tag{1}$$

where x is the mole fraction of solute, P is the pressure, P_{ref} is a standard pressure of 1 bar, ρ is the density (taken as the density of pure carbon dioxide), ρ_{ref} is the reference density for which a value of 700 kg·m^{-3} was used, and A and C are constants. The reason for using ρ_{ref} is to make the value of A much less sensitive to the experimental error in the data and to avoid the large variations caused by extraction to zero density.[24]

The constant C, resulting physically from solvation by the supercritical fluid, is assumed to be constant over the temperature range, and the constant A, arising from the vapor pressure (fugacity) of the solute, is assumed to obey the equation

$$A = a + \frac{b}{T} \tag{2}$$

where T is the absolute temperature and a and b are constants. A combination of eqs 1 and 2 will result in an overall correlation equation,

$$\ln\left(\frac{xP}{P_{\text{ref}}}\right) = a + \frac{b}{T} + C(\rho - \rho_{\text{ref}}) \tag{3}$$

In the first step, the $\ln(xP/P_{\text{ref}})$ values were plotted against density (Figure 2) for each isotherm and then were fit to a straight line by least-squares regression to obtain A and C. The plots are expected to be reasonably straight lines with similar slopes. However, the slopes show a little increase with decreasing temperature, and in general, the plots could be improved by removing the data at lower

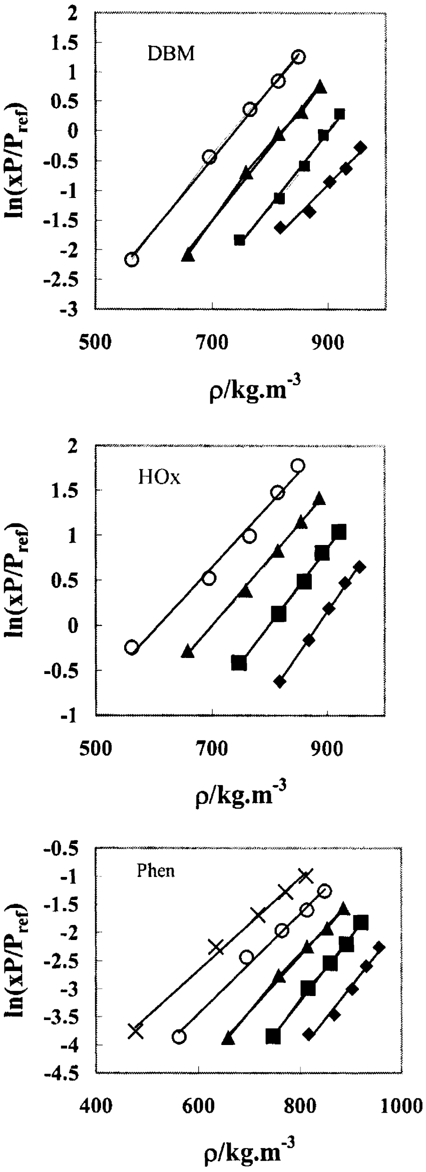


Figure 2. Plots of $\ln(xP/P_{\text{ref}})$ for DBM, HOX, and phen at isotherms of (◆) 308, (■) 318, (▲) 328, (○) 338, and (×) 348 K.

Table 2. Solubility Constants *a*, *b*, and *c* and Estimated $\Delta_{\text{sub}}H$ Values Obtained from the Data Correlation Procedure

compound	a	b/K	C/m^3 kg^{-1}	$\Delta_{\text{sub}}H$/kJ·mol^{-1}
dibenzoylmethane	28.8	−9818	0.0116	81.63
8-hydroxyquinoline	23.8	−7793	0.0081	64.80
1,10-phenanthroline	22.7	−8502	0.0100	70.69

pressures. The values of C, obtained from the slopes of the corresponding plots, were then averaged for each compound (Table 2).

By holding C constant at its average value, the experimental solubility data were then used to evaluate the A values at various temperatures for each ligand. Plots of A versus $1/T$ were then fit to straight lines (Figure 3) to obtain constants a and b for each ligand. Nice straight lines were obtained for all three ligands. The values of a and b, obtained from the plots, are also included in Table 2.

The values of a, b, and C were then used to predict the solubilities from eq 3. Figure 4 compares the calculated isotherms with the experimental data for HOX. Similar patterns were obtained for the other two ligands. As seen, the agreement is satisfactory, and the poor consistency is limited to data points obtained at the high-pressure limits of the isotherms, which are close to the melting points of the ligands. Similar results have been observed previously.[27,28] Therefore, solubilities can be confidently calculated at any temperature and pressure within the experimental range using eq 3 and the parameters listed in Table 2.

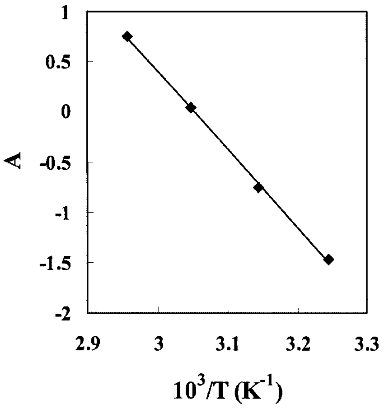


Figure 3. Plots of A versus $^1/_T$ for HOX.

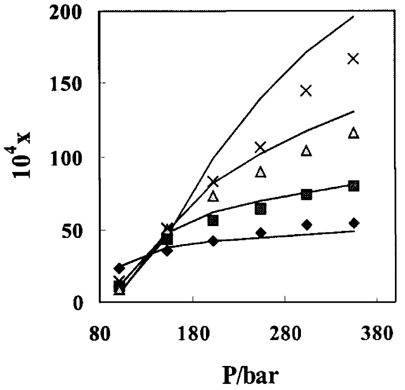


Figure 4. Comparison of experimental (points) and calculated (lines) solubilities at various temperatures for HOX.

Parameter b is approximately related to the enthalpy of sublimation of the solid solutes $\Delta_{\text{sub}}H$ by[28]

$$\Delta_{\text{sub}}H = -Rb \tag{4}$$

where R is the gas constant. The validity of eq 4 relies on the assumption that the enhancement factor $\ln(xP/P_v)$, where P_v is the vapor pressure of the solid solute, is independent of temperature. This assumption has been found to be nearly true in practice. The estimated $\Delta_{\text{sub}}H$ values are also included in Table 2.

Literature Cited

(1) Choi, S. Y.; Yoshida, Z.; Ohashi, K. Supercritical Carbon Dioxide Extraction Equilibrium of Gallium(III) with 2-Methyl-8-quinolinol and 2-Methyl-5-butyloxymethyl-8-quinolinol. *Talanta* **2002**, *56*, 689−697.

(2) Lin, Y.; Wu, H.; Smart, N. G.; Wai, C. M. Studies on In-Situ Chelation/Supercritical Fluid Extraction of Lanthanides and Actinides Using a Radiotracer Technique. *Sep. Sci. Technol.* **2001**, *36*, 1149−1162.

(3) Elshani, S.; Smart, N. G.; Lin, Y.; Wai, C. M. Application of Supercritical Fluids to the Reactive Extraction and Analysis of Toxic Heavy Metals from Environmental Matrices-System Optimization. *Sep. Sci. Technol.* **2001**, *36*, 1197−1210.

(4) Sun, Y. C.; Chung, Y. T.; Mierzwa, J. Study of Matrix Influence on Supercritical Fluid Extraction of Polar Mercury Species from Solid Samples. *Analyst* **2001**, *126*, 1694−1699.

(5) Tomioka, O.; Meguro, Y.; Iso, S.; Yoshida, Z. New Method for Removal of Uranium from Solid Wastes with Supercritical CO_2

Medium Containing HNO_3−TBP Complex. *J. Nucl. Sci. Technol.* **2001**, *38*, 461−462.
(6) Burford, M. D.; Ozel, M. Z.; Clifford, A. A.; Bartle, K. O.; Lin, Y.; Wai, C. M.; Smart, N. G. Extraction and Recovery of Metal Using a Supercritical Fluid with Chelating Agents. *Analyst* **1999**, *124*, 609−614.
(7) Fog, G. P.; Pacey, G. E. Specific Extraction of Chromium(VI) Using Supercritical Fluid Extraction. *Talanta* **2000**, *51*, 339−347.
(8) Otu, E. O.; Wilson, J. J. Supercritical Carbon Dioxide Elution of Gold−Cyanide Complex from Activated Carbon. *Sep. Sci. Technol.* **2000**, *35*, 1879−1886.
(9) Ashraf-Khorassani, M.; Taylor, L. T. Supercritical Fluid Extraction of Mercury(II) Complexes from Different Matrices. *Anal. Chim. Acta* **1999**, *379*, 1−9.
(10) Smart, N. G.; Carleson, T. E.; Elshani, S.; Wang, S.; Wai, C. M. Extraction of Toxic Heavy Metals Using Supercritical Fluid Carbon Dioxide Containing Organophosphorus Reagents. *Ind. Eng. Chem. Res.* **1997**, *36*, 1819−1826.
(11) Wai, C. M.; Wang, S.; Liu, Y.; Lopez-Avila, V.; Beckert, W. F. Evaluation of Dithiocarbamate and β-Diketones as Chelating Agents in Supercritical Fluid Extraction of Cd, Pb, and Hg from Solid Samples. *Talanta* **1996**, *43*, 2083−2091.
(12) Cross, W.; Akgerman, A.; Erkey, C. Determination of Metal−Chelate Complex Solubilities in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1996**, *35*, 1765−1770.
(13) Ashraf-Khorassani, M.; Combs, M. T.; Taylor, L. T. Solubility of Metal Chelates and Their Extraction from an Aqueous Environment via Supercritical CO_2. *Talanta* **1997**, *44*, 755−763.
(14) Smart, N. G.; Carleson, T.; Kast, T.; Clifford, A. A.; Burford, N. D.; Wai, C. M. Solubility of Chelating Agents and Metal-Containing Compounds in Supercritical Fluid Carbon Dioxide. *Talanta* **1997**, *44*, 137−150.
(15) Palo, D. R.; Erkey, C. Solubility of Dichlorobis(triphenylphosphine) Nickel (II) in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1998**, *43*, 47−48.
(16) Ozel, M. Z.; Bartle, K. D.; Clifford, A. A.; Burford, M. D. Extraction, Solubility and Stability of Metal Complexes Using Stainless Steel Supercritical Fluid Extraction System. *Anal. Chim. Acta* **2000**, *417*, 177−184.
(17) Minczewski, J.; Chwastowska, J.; Dybczynski, R. Separation and Preconcentration Methods in Inorganic Trace Analysis: Ellis Horwood Ltd.: Chichester, U.K., 1982.
(18) Shamsipur, M.; Ghiasvand, A. R.; Yamini, Y. Solid-Phase Extraction of Ultratrace Uranium(VI) in Natural Waters Using Octadecyl Silica Membrane Disks Modified by Tri-*n*-Octylphosphine Oxide and Its Spectrophotometric Determination with Dibenzoylmethane. *Anal. Chem.* **1999**, *71*, 4892−4895.
(19) Marczenko, Z. Separation and Spectrophotometric Determination of Elements; Elis Harwood: London, 1986.
(20) Onishi, H. Photometric Determination of Traces of Metals, 4th ed. Wiley: New York, 1989; Part IIB.
(21) Koh, T.; Sugimoto, T. Extractive Spectrophotometric Determination of Silver(I) at the 10^{-7} M Level Using 1,10-Phenanthroline and Tetrabromophenolphthalein Ethyl Ester. *Anal. Chim. Acta* **1996**, *333*, 167−173.
(22) Zahir, M. H.; Masuda, Y. Extractive Separation of Trivalent Lanthanide Metals with a Combination of Di(2-ethylhexyl)-phosphoric Acid and 1,10-Phenanthroline. *Talanta* **1997**, *44*, 365−371.
(23) Bartle, K. D.; Clifford, A. A.; Jafar, S. A.; Shiltone, G. F. Solubilities of Solids and Liquids of Low Volatility in Supercritical Carbon Dioxide. *J. Phys. Chem. Ref. Data* **1991**, *20*, 613−716.
(24) Safa-Ozcan, A.; Clifford, A. A.; Bartle, K. D. Solubility of Disperse Dyes in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1997**, *42*, 590−592.
(25) Yamini, Y.; Fat'hi, M. R.; Alizadeh, N.; Shamsipur, M. Solubility of Dihydroxybenzene Isomers in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1998**, *152*, 299−305.
(26) Fat'hi, M. R.; Yamini, Y.; Sharghi, H.; Shamsipur, M. Solubilities of Some 1,4-Dihydroxy-9,10-anthraquinone Derivatives in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1998**, *43*, 400−402.
(27) Yamini, Y.; Bahramifar, N. Solubility of Polycyclic Aromatic Hydrocarbons in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **2000**, *45*, 53−56.
(28) Miller, D. J.; Hawthorn, S. B.; Clifford, A. A.; Zhu, S. Solubility of Polycyclic Aromatic Hydrocarbons in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1996**, *41*, 779−786.

Received for review May 25, 2003. Accepted June 4, 2004.

JE034098J