J. Chem. Eng. Data **1995,** *40,* 1217−1221

Solubility of Ferrocene and a Nickel Complex in Supercritical Fluids

Catherine M. Cowey, Keith D. Bartle, Mark D. Burford, Anthony A. Clifford,* and Shuang Zhu

School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

Neil G. Smart and Nigel D. Tinker

Company Research Laboratory, British Nuclear Fuels plc, Springfields Works, Salwick, Preston PR4 0XJ, U.K.

Supercritical fluid extraction of metals in the presence of complexing agents for environmental monitoring, cleanup, and metals processing is now being extensively researched, and there is a need for solubility data of metal complexes. In this paper, the method used is the combination of a study of chromatographic retention over a wide range of pressures at 40, 50, 60, and 70 °C, followed by selected direct solubility measurements, to provide a comprehensive set of solubility results obtained with minimum effort. The method relies on the assumption that an inverse relationship exists between chromatographic retention and solubility in the mobile phase. This assumption is checked in this study. Results are presented for the solubility of ferrocene in supercritical carbon dioxide and a nickel complex, (5,7,12,14-tetramethyl-2,3:9,10-dibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine)nickel(II)], in supercritical carbon dioxide modified with 10 vol % methanol.

Introduction

Supercritical fluid extraction (SFE) of metals is now being regarded as a serious possibility, with potential applications in the analysis of environmental samples, for the cleanup of metal-contaminated industrial sites, and for the processing of metal ores and separation of metal mixtures. In order for the metal ions to be soluble in environmentally friendly solvents such as pure and modified supercritical carbon dioxide, the metal ions must be present as electrically neutral complexes, and this gives rise to the possibility of selective extraction due to the different affinity of particular complexing agents for different metal ions. In this context, a considerable amount of work has been carried out in the supercritical fluid chromatography (SFC) of metal complexes (Carey et al., 1994; Iso et al., 1994; Blake et al., 1994; Chester et al., 1994), supercritical fluid solubility of metal complexes (Laintz et al., 1991; Johnston and Lemert, 1991; Beckman et al., 1993; Marshall and Wang, 1994), and SFE of metal compounds in the presence of complexing agents (Chester et al., 1994; Brauer et al., 1994; Laintz and Tachikawa, 1994; Alzaga et al., 1994; Alcaraz et al., 1994). For the design of an analytical process, detailed knowledge of solubility is required, and this paper gives an economical method for measuring these data.

The degree of retention of a solute in SFC, as measured by the capacity fadctor, k', is at least qualitatively inversely related to the solvating power of the mobile phase for that solute: the more soluble it is in the mobile phase, the less it will be retained. In some situations at constant temperature, the solubility of solid solutes in the mobile phase can to a good approximation be inversely proportional to the capacity factor (Bartle et al., 1988; Bartle et al., 1989). When this is the case, chromatographic retention can be used to measure solubilities relatively rapidly, and this has been used for supercritical fluids. In one study, chromatographic retention has been used to obtain pressure thresholds for the solubilities of various compounds at different temperatures (Smith et al., 1987). In another, solubilities have been obtained at lower pressures in a supercritical fluid by using retention measurements and vapor pressure measurements (Barker et al., 1988), also used to obtain the solubility of some polyaromatic hydrocarbons in supercritical carbon dioxide (Bartle et al., 1990). The relationship used is

$$S = C/k' \tag{1}$$

where S is the solubility (per unit volume), k' is the chromatographic capacity factor defined in terms of the retention volume, V_R, and the void volume of the column and the connecting tubes, V_m, by

$$k' = \frac{(V_R - V_M)}{V_M} \tag{2}$$

and C is a constant for a particular column, solute, and temperature, given by

$$C = A_{\exp}[B/RT] \tag{3}$$

In eq 3, A and B are constants for a particular column and temperature. The validity of eqs 1 and 3 relies on assumptions, justifiable in particular circumstances which have been discussed previously (Bartle et al., 1990). However, the validity of these equations can be tested by making a limited number of direct solubility measurements to obtain values of C at various temperatures, to check that C is indeed a constant at a particular temperature, and to show that C obeys eq 3 over a range of temperature. Having checked the validity of these equations and obtained values of C, a relatively rapid series of SFC experiments can then be made to generate solubilities from eq 1. In practice and for convenience, as seen below, the quantity $S\ (V_R - V_M) = CV_M$, rather than C, is calculated, as V_M is also a constant for a particular column and chromatograph and the same arguments apply.

Experimental Section

SFC was carried out on a packed column chromatograph (Hewlett-Packard), fitted with a variable flow valve, al-

0021-9568/95/1740-1217$09.00/0

Table 1. Directly Measured Solubilities, S_d, Retention Volumes, V_R, and Values of the Constant CV_M for Ferrocene in Supercritical Carbon Dioxide

conditions	S_d/(g mL^{-1})	V_R/mL	CV_M/mg
134.1 bar, 40 °C	4.77×10^{-3}	4.23	7.68×10^{-3}
244.4 bar, 40 °C	9.13×10^{-3}	3.42	7.31×10^{-3}
335.5 bar, 40 °C	1.21×10^{-2}	3.28	8.04×10^{-3}
			av: 7.68×10^{-3}
134.1 bar, 50 °C	3.80×10^{-3}	5.05	9.61×10^{-3}
244.4 bar, 50 °C	1.11×10^{-2}	3.51	1.10×10^{-2}
335.5 bar, 50 °C	1.33×10^{-2}	3.15	8.40×10^{-3}
			av: 9.68×10^{-3}
134.1 bar, 60 °C	2.42×10^{-3}	7.09	1.07×10^{-2}
244.4 bar, 60 °C	1.30×10^{-2}	3.60	1.20×10^{-2}
335.5 bar, 60 °C	1.75×10^{-2}	3.19	9.11×10^{-3}
			av: 1.06×10^{-2}
134.1 bar, 70 °C	1.38×10^{-3}	10.40	1.05×10^{-2}
244.4 bar, 70 °C	1.49×10^{-2}	3.63	1.24×10^{-2}
335.5 bar, 70 °C	2.07×10^{-2}	3.18	8.15×10^{-3}
			av: 1.03×10^{-2}

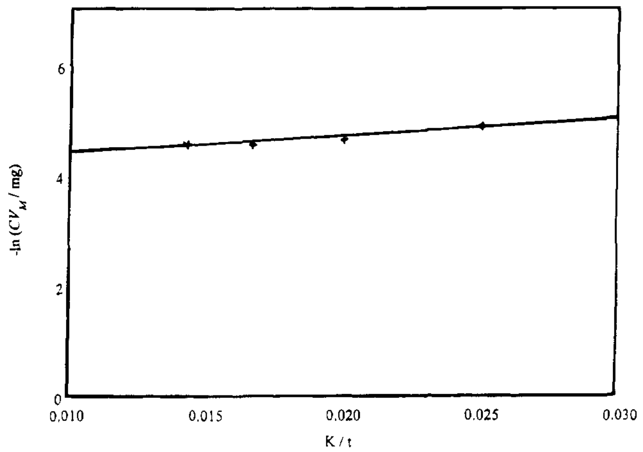

Figure 1. Temperature dependence of CV_M for ferrocene in supercritical carbon dioxide.

lowing a constant flow rate, pressure, and temperature to be maintained. Samples were introduced *via* a timed-split injection valve using a 5 μL sample loop.

Ferrocene obtained from the Aldrich Chemical Co., 98 % pure, was used for SFC as a 1.072 g dm^{-3} (5.76×10^{-3} mol dm^{-3}) solution of ferrocene in heptane (Fisons HPLC grade). For the measurements on ferrocene, a flow rate of 2.0 mL min^{-1} (measured at the pump) of CO_2 (BOC speciality gases, liquid withdrawal, without helium head pressure) was used with an octyldecylsilyl-bonded silica (5 μm) column (Hewlett-Packard, Hypersil, P/N 799160D-574, 200 mm long with 4.6 mm internal diameter). Retention times for ferrocene were obtained at average pressures over the column from 97 to 366 bar and temperatures of 40, 50, 60, and 70 °C.

A nickel complex, 5,7,12,14-tetramethyl-2,3:9,10-dibenzo-[*b*,*i*][1,4,8,11]tetraazacyclotetradecine)nickel (II), synthesized at British Nuclear Fuels was used as a 2.406 g dm^{-3} (6.00×10^{-3} mol dm^{-3}) solution in chloroform (Fisons HPLC grade). Anal. Calcd for $Ni[C_{22}H_{22}N_4]$: C, 65.87; H, 5.53; N, 13.97. Found: C, 66.32; H, 5.61; N, 13.88. ^1H NMR ($CDCl_3$, chemical shifts in freshly prepared solutions (δ, ppm, relative to TMS)): complex pattern, 6.73, 6.72, 6.71, 6.69, 6.60, 6.58, 6.57, 6.56 (8H, aromatic); 4.88 (2H, methylene); 2.10 (12H, methyl). For the nickel complex, a similar combined flow rate of 2.0 mL min^{-1} of 10 vol % methanol (Fisons HPLC grade) modified CO_2 and flowed into a similar octyldecylsilyl-bonded silica (5 μm) column (phase separations, S5ODS2 142632, 250 mm long with 4.6 mm internal diameter). Retention times for the nickel complex were obtained at average pressures over the column of 161–372 bar and the same temperatures as for ferrocene.

Pressure drops along the columns were 30–40 bar, and the average pressure was used in presenting the results. The effect of a pressure drop along the column on densities and capacity factors has been discussed (Bartle et al., 1989). It was shown that this is most important near the critical density, and at 134 bar and 70 °C (the worst case) a 2% error would be introduced. Retention times were converted to retention volumes using volume flow rates on the column obtained from pump flow rates, and densities obtained from a published equation of state for pure carbon dioxide (Span and Wagner) and the Peng–Robinson equation of state for the methanol–CO_2 mixtures (loaded on the instrumental software of the SFC) were used. Values of 2.65 and 6.73 mL were used for V_M for the ferrocene and nickel complex work, respectively.

Direct solubility measurements were obtained using an SFE system built in-house consisting of a dual pumping system (ISCO Model 100D syringe pumps), extraction cell, and solvent-trapping system. The ISCO syringe pump has on electronically controlled stepping motor which gives a high flow rate accuracy. Errors in flow rate mostly result from the error in the density of the fluid in the pumps which is estimated to be ±0.5%. The efficiency of the solvent trap was evaluated (Bartle et al., 1995). The pure metal complex was loaded in the extraction cell mixed with glass beads (Alltech Associates, 60/80), and pure CO_2 or 10 vol % methanol modified CO_2 flowed through the cell with a flow rate of 0.2 mL min^{-1}, measured as liquid at the pump at 5 °C. Temperatures were indicated on the controls of the commercial oven, were checked using a thermometer, and were found to be accurate to ±0.5 °C. The accuracy of the pressure measurement devices was ±2% of the full scale of the pump, and the pressure measurement devices were calibrated before any solubility measurements were taken. After equilibrium had been reached, the solution of the metal complex, trapped in methanol for ferrocene and chloroform for the nickel complex, was collected for periods of 15 min and the total amount of the complex obtained in each period determined by UV absorption. The amount of supercritical fluid was determined by the flow rate and density at the pump(s) and the solubility in terms of grams per unit volume of supercritical fluid using calculated densities in the extraction cell as used above. An average of at least four experiments was used for each solubility determination.

Results and Discussion

Ferrocene. Direct Solubility Measurements. Direct measurements of the solubility of ferrocene in pure supercritical carbon dioxide were made at three pressures at each of four temperatures to cover the range of SFC measurements and are given in the second column of Table 1. The precision of direct solubility measurements was determined by obtaining the percentage relative standard deviation of the four measurements; this averaged ±3% and varied from 0.4% to 9.1% in the worst case.

Values of the Constant CV_M. SFC retention measurements were carried out at the same temperatures as the direct solubility measurements over a range of pressures. Those results at the same pressure as the direct solubility measurements are given in the third column of Table 1. The quantities $S(V_R - V_M) = CV_M$ are then calculated and given in the fourth column. Agreement of the values is obtained at a given temperature, indicating the validity of eq 1. Average values for CV_M were then obtained at each temperature and are also given in Table 1. To check the

Table 2. Solubilities (g mL^{-1}) Obtained by Retention, S_c, and Directly, S_d, for Ferrocene in Supercritical Carbon Dioxide

	40 °C		50 °C		60 °C		70 °C	
P/bar	S_c	S_d	S_c	S_d	S_c	S_d	S_c	S_d
97.5	2.07×10^{-3}		5.82×10^{-4}		3.01×10^{-4}		2.22×10^{-4}	
117.3	3.86×10^{-3}		2.13×10^{-3}		1.06×10^{-3}		5.94×10^{-4}	
134.1	5.04×10^{-3}	4.77×10^{-3}	3.84×10^{-3}	3.80×10^{-3}	2.29×10^{-3}	2.42×10^{-3}	1.41×10^{-3}	1.38×10^{-3}
153.9	6.29×10^{-3}		5.47×10^{-3}		3.95×10^{-3}		2.75×10^{-3}	
183.9	7.82×10^{-3}		7.50×10^{-3}		6.45×10^{-3}		5.36×10^{-3}	
214.1	8.89×10^{-3}		9.27×10^{-3}		8.58×10^{-3}		8.34×10^{-3}	
244.4	1.03×10^{-2}	9.13×10^{-3}	1.07×10^{-2}	1.11×10^{-2}	1.07×10^{-2}	1.30×10^{-2}	1.12×10^{-2}	1.49×10^{-2}
274.9	1.16×10^{-2}		1.23×10^{-2}		1.30×10^{-2}		1.48×10^{-2}	
305.0	1.31×10^{-2}		1.36×10^{-2}		1.48×10^{-2}		1.74×10^{-2}	
335.5	1.27×10^{-2}	1.21×10^{-2}	1.84×10^{-2}	1.33×10^{-2}	1.88×10^{-2}	1.75×10^{-2}	2.05×10^{-2}	2.07×10^{-2}
366.3	1.48×10^{-2}		2.06×10^{-2}		2.26×10^{-2}		2.40×10^{-2}	

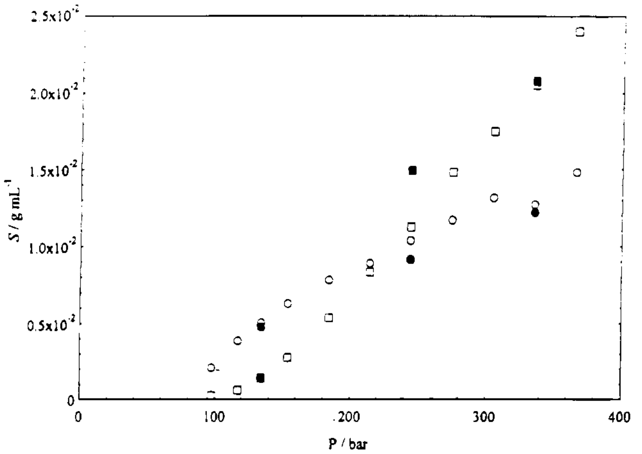

Figure 2. Solubility, S, of ferrocene in supercritical carbon dioxide at (○) 40 °C and (□) 70 °C obtained using chromatography. The solid symbols show direct measurements for comparison.

validity of eq 3, values of ln CV_M, using the averaged values, are plotted versus $1/T$ in Figure 1, and a reasonable straight line is obtained.

Solubility Results Obtained from Chromatography. Using the calculated average values of CV_M, from Figure 1, the total range of values of V_R, obtained from SFC were converted to solubility data, S_c, and are shown in Table 2. Comparison is made with direct solubility measurements, S_d, for each isotherm, to indicate accuracy. Figure 2 gives plots of the highest and lowest isotherms. Differences between direct an indirect solubility measurements give an indication of the overall experimental error. For nine of the points this averaged 4.5%. For three of the points high differences were obtained, indicating that these measurements should be given less importance. The overall error in the nine direct measurements and all the indirect measurements we believe to be around ±9%.

Nickel Complex. Direct Solubility Measurements and Values of the Constant CV_M. Using the same procedure as for ferrocene, measurements for the nickel complex in supercritical carbon dioxide modified with 10 vol % methanol were obtained and are given in Table 3. For the nickel complex the percentage relative standard deviation of the four direct solubility measurements averaged ±6% and varied from 2% to 13% in the worst case. Values of CV_M were also calculated and given in the fourth column and again can be seen to be reasonably constant at a given temperature. Average values of CV_M were then calculated and are given in Table 3. Again the validity of eq 3 was checked by plotting values of average ln CV_M versus $1/T$ in Figure 3, and a reasonably straight line is obtained.

Solubility Results Obtained from Chromatography. Solubilities, S_c, were then calculated using the average values of CV_M and a range of retention volume data. A comparison of calculated solubilities, S_c, and directly measured solubilities, S_d, is given in Table 4. Figure 4 gives plots of the highest and lowest isotherms of solubility. For the nickel complex for nine of the points the overall experimental error averaged 7%. For three of the points high differences were obtained, indicating that these measurements should be given less importance. The overall error in the nine direct measurements and all the indirect measurements we believe to be around ±14%.

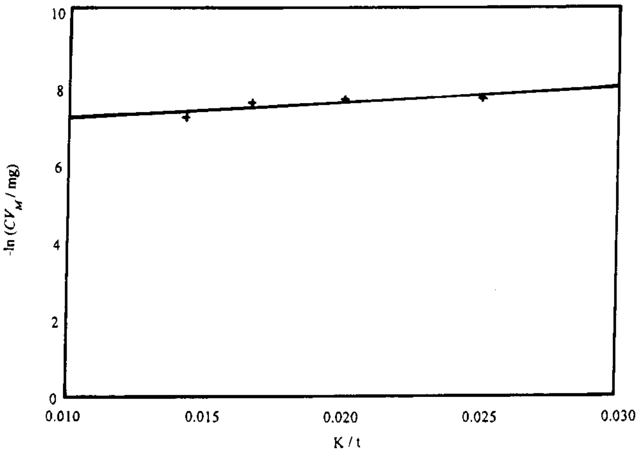

Figure 3. Temperature dependence of CV_M for the nickel complex in supercritical carbon dioxide modified with 10 vol % methanol.

Table 3. Directly Measured Solubilities, S_d, Retention Volumes, V_R, and Values of the Constant CV_M for the Nickel Complex in 10 vol % Methanol Modified Supercritical Carbon Dioxide

conditions	S_d/(g mL^{-1})	V_R/mL	CV_M/mg
161.1 bar, 40 °C	1.05×10^{-5}	50.39	4.58×10^{-4}
252.6 bar, 40 °C	1.70×10^{-5}	32.20	4.35×10^{-4}
342.3 bar, 40 °C	2.20×10^{-5}	26.86	4.43×10^{-4}
			av: 4.45×10^{-4}
161.1 bar, 50 °C	1.00×10^{-5}	55.22	4.84×10^{-4}
252.6 bar, 50 °C	2.01×10^{-5}	29.82	4.66×10^{-4}
342.3 bar, 50 °C	2.45×10^{-5}	25.36	4.57×10^{-4}
			av: 4.69×10^{-4}
161.1 bar, 60 °C	8.02×10^{-6}	67.95	4.91×10^{-4}
252.6 bar, 60 °C	2.44×10^{-5}	28.89	5.42×10^{-4}
342.3 bar, 60 °C	3.13×10^{-5}	21.90	4.75×10^{-4}
			av: 5.02×10^{-4}
161.1 bar, 70 °C	7.21×10^{-6}	97.14	6.52×10^{-4}
252.6 bar, 70 °C	3.44×10^{-5}	30.05	8.04×10^{-4}
342.3 bar, 70 °C	5.77×10^{-5}	18.98	7.07×10^{-4}
			av: 7.21×10^{-4}

Correlation of the Solubility Data. Supercritical fluid solubilities are difficult to predict and correlate, and so a simple method (Bartle et al., 1991) was used to correlate the data presented here. Although the fit to the data is not as good as could be desired, only three

Table 4. Solubilities (g mL^{-1}) Obtained by Retention, S_c, and Directly, S_d, for the Nickel Complex in 10 vol % Methanol Modified Supercritical Carbon Dioxide

	40 °C		50 °C		60 °C		70 °C	
P/bar	S_c	S_d	S_c	S_d	S_c	S_d	S_c	S_d
161.1	9.53×10^{-6}	1.05×10^{-5}	1.04×10^{-5}	1.00×10^{-5}	9.37×10^{-6}	8.02×10^{-6}	6.96×10^{-6}	7.21×10^{-6}
191.6	1.18×10^{-5}		1.41×10^{-5}		1.46×10^{-5}		1.29×10^{-5}	
221.9	1.41×10^{-5}		1.80×10^{-5}		2.01×10^{-5}		1.96×10^{-5}	
252.6	1.63×10^{-5}	1.70×10^{-5}	2.18×10^{-5}	2.01×10^{-5}	2.59×10^{-5}	2.44×10^{-5}	2.69×10^{-5}	3.44×10^{-5}
283.3	1.83×10^{-5}		2.55×10^{-5}		3.16×10^{-5}		3.49×10^{-5}	
314.0	1.99×10^{-5}		2.64×10^{-5}		3.72×10^{-5}		4.31×10^{-5}	
342.3	2.06×10^{-5}	2.20×10^{-5}	2.70×10^{-5}	2.45×10^{-5}	3.78×10^{-5}	3.13×10^{-5}	5.13×10^{-5}	5.77×10^{-5}
372.3	2.01×10^{-5}		2.65×10^{-5}		3.85×10^{-5}		5.59×10^{-5}	

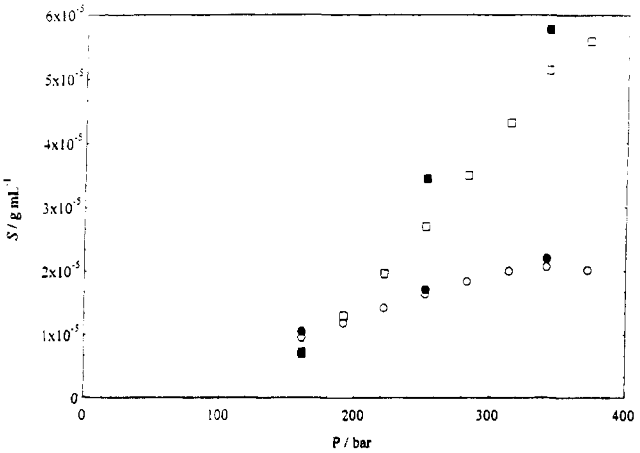

Figure 4. Solubility of the nickel complex in supercritical carbon dioxide modified with 10 vol % methanol at (○) 40 °C and (□) 70 °C obtained using chromatography. The solid symbols show direct measurements for comparison.

Table 5. Parameters To Be Used in Predicting Solubilities from Eqs 4 and 5

complex	BB/(kg m^{-3})	a	b/K^{-1})
ferrocene	0.0838	17.6	6090
nickel complex	0.0192	19.3	9810

parameters for each compound are needed to predict a value at any pressure and temperature in the experimental range.

The correlation equation used is

$$\ln(xp/p^0) = A' + B'(\rho - \rho_{\text{ref}}) \tag{4}$$

where x is the mole fraction solubility, p is the pressure, p^0 is a standard pressure of 1 bar, and ρ is the density of the solution (which is approximated by the density of the pure solvent). ρ_{ref} is a reference density for which a value of 700 kg m^{-3} was used here. This is used so that the value of A' refers to a density close to the experimental values, avoiding the large variations caused by extrapolation to zero density. B' is a constant, and A' is given by

$$A' = a + b/T \tag{5}$$

The fitting procedure used was to fit each isotherm by least squares to eq 4 to obtain values of A' and B'. The values of B' were then averaged for each compound, and the values given in Table 5 were obtained. Using these averaged values of B' the isotherms were then refitted to obtain new best values of A'. These values were then plotted against $1/T$ for each compound, as shown in Figures 5a and 6a, and values for a and b were obtained from a least-squares fit of eq 5, which are given in Table 5. For these calculations a published equation of state for pure carbon dioxide (Span and Wagner, 1995) and the Peng-Robinson equation of state for the carbon dioxide and methanol (loaded on the instrumental software of the supercritical fluid chromatograph) were used.

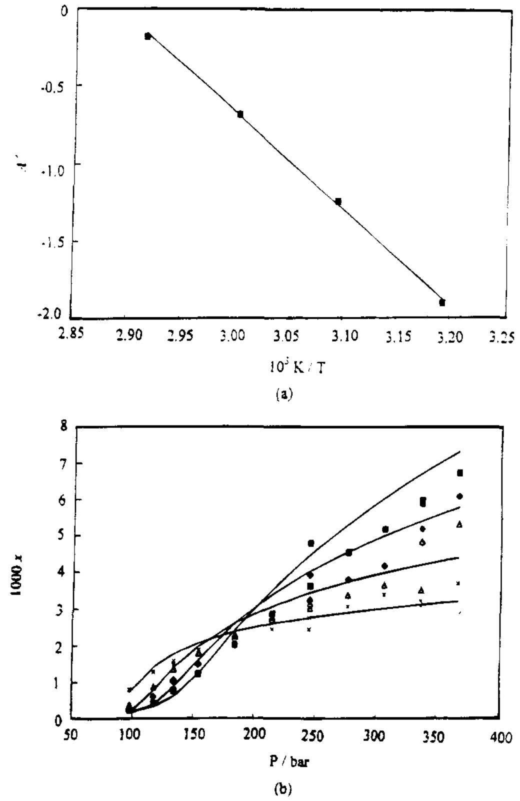

Figure 5. Correlation of the solubility in mole fraction, x, for ferrocene. Graph a shows a plot of A' versus $1/T$. Graph b shows comparison of predicted curves (lines) and experimental points: (■) 70 °C; (◆) 60 °C; (△) 50 °C; (×) 40 °C.

Finally, using eqs 4 and 5 and the parameters in Table 5, predicted solubilities were compared with experimental values in Figures 5b and 6b. Although the fitting of individual isotherms to eq 4 was very good, averaging of the parameters to predict the whole temperature range is less successful, as can be seen. However, the equations give a ready method of obtaining approximate solubilities at any temperature and pressure (density).

Conclusions

This study demonstrates the feasibility of obtaining a large number of reasonable quality solubility results in supercritical fluids, using rapid chromatographic measurements and a small number of direct measurements. For both ferrocene and the nickel complex there is a good agreement between directly measured solubilities (S_d) and chromatographic retention solubilities (S_c). The method was found to be applicable to a complex whose solubility was known to be high and one with much lower solubility, requiring a modifier. The precision of the results is estimated to vary from 5% at low pressures to 20% at

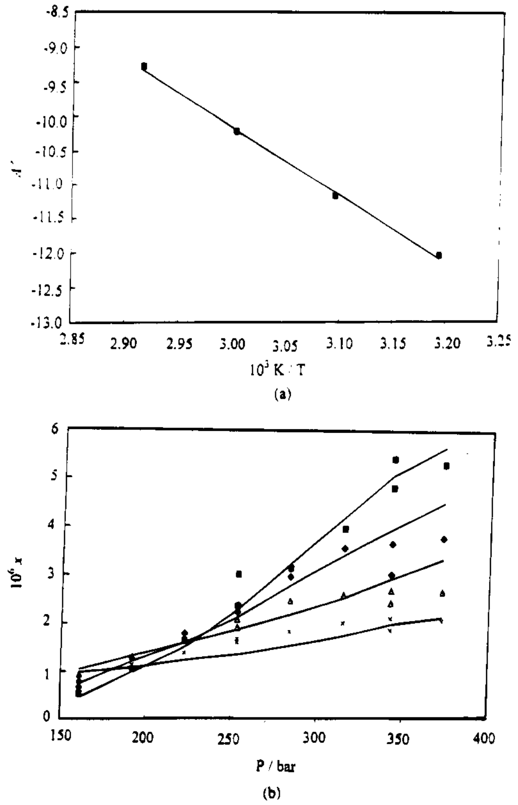

Figure 6. Correlation of the solubility in mole fraction, x, for the nickel complex. Graph a shows a plot of A' versus $1/T$. Graph b shows comparison of predicted curves (lines) and experimental points: (■) 70 °C; (◆) 60 °C; (△) 50 °C; (×) 40 °C.

higher pressures, where high solubilities and low retention times give rise to higher experimental errors.

The results indicate that the ferrocene complex is more soluble than the nickel complex at similar temperatures and pressures. Indeed, the nickel complex is essentially insoluble in pure supercritical carbon dioxide and requires the addition of 10 vol % methanol to achieve a measurable solubility. These results can be interpreted in terms of the respective structure of the two compounds.

Ferrocene is a bis(p-cyclopentadienyl)iron complex, (p-C_5H_5)$_2$Fe, in which all the metal 3d, p, and s orbitals are participating in bonding to the cyclopentadienyl ligands. All the molecular bonding orbitals are filled such that no free coordination sites are available on the iron, resulting in ferrocene having properties resembling those of aromatic compounds. This includes high solubility in nonpolar solvents.

The structure of the nickel complex is rather different, since the metal ion is not as effectively "wrapped up" by the ligand as in the ferrocene case. The complex is a near square planar system, with all but the $3d_{x^2y^2}$ orbital involved in bonding. The coordinatively unsaturated "faces" of the nickel probably account for its very low solubility in pure supercritical carbon dioxide.

It is possible for planar Ni(II) complexes to react with adducts to form octahedral MXL_2 systems. Presumably the increase in solubility of the nickel complex when a modifier is present is due to methanol solvating the two available trans sites, and hence reducing the polarity of the complex. However, the metal is still not as effectively enveloped by the ligand as for iron, as indicated by the low solubility compared to ferrocene.

Literature Cited

Alcaraz, M.; Beckert, W. F.; Lopez-Avila, V.; Liu, Y. Off-Line Complexation/Supercritical Fluid Extraction and Gas Chromatography with Atomic Emission Detection for the Determination and Speciation of Organotin Compounds in Soils and Sediments. *Anal. Chem.* **1994**, *66*, 3788–3796.

Alzaga, R.; Bayona, J. M.; Cai, Y. In Situ Derivatization and Supercritical Fluid Extraction for the Simultaneous Determination of Butyltin and Phenyltin Compounds in Sediment. *Anal. Chem.* **1994**, *66*, 1161–1167.

Barker, I. K.; Bartle, K. D.; Clifford, A. A. Measurement of solubilities in Fluids at Supercritical Temperatures and Lower Pressures using Chromatographic Retention. *Chem. Eng. Commun.* **1988**, *68*, 177–184.

Bartle, K. D.; Boddington, T.; Clifford, A. A.; Shilstone, G. F. Effect of Pressure Drop Across the Column on Average Densities and Capacity Factors in Supercritical Fluid Chromatography. *J. Chromatogr.* **1989**, *471*, 347–355.

Bartle, K. D.; Burford, M. D.; Clifford, A. A.; Cowey, C. M. Variable Flow Control and Collection Device for Use with Supercritical Fluids. *J. Chromatogr.* **1995**, submitted for publication.

Bartle, K. D.; Clifford, A. A.; Jafar, S. A. Measurement of Solubility in Supercritical Fluids Using Chromatographic Retention: the Solubility of Fluorene, Phenanthrene, and Pyrene in Carbon Dioxide. *J. Chem. Eng. Data* **1990**, *35*, 355–360.

Bartle, K. D.; Clifford, A. A.; Jafar, S. A. Solubilities of solids and Liquids of Low Volatility in Supercritical Carbon dioxide. *J. Phys. Chem. Ref. Data* **1991**, *20*, 713–757.

Bartle, K. D.; Clifford, A. A.; Kithinji, J. P.; Shilstone, G. F. Studies of the Temperature Dependence of Retention in Supercritical Fluid chromatography. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 4487–4493.

Beckman, E. J.; Beitle, R. R.; Enick, R. M.; Hoefling, T. A. Design and Synthesis of Highly CO_2-Soluble Surfactants and Chelating Agents. *Fluid Phase Equilib.* **1993**, *83*, 203–212.

Blake, E.; Cornell, D.; Raynor, M. W. Determination of organotin compounds by capillary supercritical fluid chromatography with inductively coupled plasma mass spectrometric detection. *J. Chromatogr.* **1994**, 683, 223–231.

Brauer, R. D.; Jean, F. M.; Lin, Y.; Wai, C. M. Supercritical Fluid Extraction of Thorium and Uranium Ions from Solid and Liquid Materials with Fluorinated β-Diketones and Tributyl Phosphate. *Environ. Sci. Technol.* **1994**, *28*, 1190–1193.

Carey, J. M.; Caruso, J. A.; Vela, N. P. Chromium determination by supercritical fluid chromatography with inductively coupled plasma mass spectrometric and flame ionization detection. *J. Chromatogr.* **1994**, *662*, 329–340.

Chester, T. L.; Pinkston, J. D.; Raynie, D. E. Supercritical Fluid Chromatography and Extraction. *Anal. Chem.* **1994**, *66*, 106R–130R.

Iso, S.; Laintz, K. E.; Meguro, Y., Yoshida, Z. Super Fluid Chromatographic Behavior of Lanthanide β-Diketonates. *J. High Resolut. Chromatogr.* **1994**, *17*, 603–606.

Johnston, K. P.; Lemert, R. M. Chemical Complexing Agents for Enhanced Solubilities in Supercritical Fluid Carbon Dioxide. *Ind. Eng. Chem. Res.* **1991**, *30*, 1222–1231.

Laintz, K. E.; Tachikawa, E. Extraction of Lanthanides from Acidic Solution Using Tributyl Phosphate Modified Supercritical Carbon Dioxide. *Anal. Chem.* **1994**, *66*, 2190–2193.

Laintz, K. E.; Smith, R. D.; Wai, C. M.; Yonker, C. R. Solubility of Fluorinated Metal Diethyldithiocarbamates in supercritical Carbon Dioxide. *J. Supercrit. Fluids* **1991**, *4*, 194–198.

Marshall, W. D.; Wang, J. Recovery of Metals from Aqueous Media by Extraction with Supercritical Carbon Dioxide. *Anal. Chem.* **1994**, *66*, 1658–1663.

Smith, R. D.; Usdeth, H. R.; Wright, B. W.; Yonker, C. R. Solubilities in Supercritical Fluids: The Application of Chromatographic Measurement Methods. *Sep. Sci. Technol.* **1987**, *22*, 1065–1086.

Span, R.; Wagner, W. *J. Phys. Chem. Ref. Data* **1995**, submitted for publication.

Received for review April 21, 1995. Accepted August 16, 1995.® Financial support from an EPSRC award from British Nuclear Fuels plc is gratefully acknowledged.

JE950095Y

® Abstract published in *Advance ACS Abstracts,* October 15, 1995.