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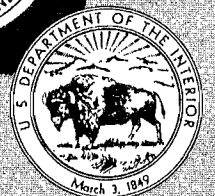
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REPORT OF INVESTIGATIONS/1989

Supercritical CO₂ Solubility of TiCl₄

By W. K. Tolley and L. S. Tester

BUREAU OF MINES



UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere, standard	mL	milliliter
°C	degree Celsius	mol	mole
h	hour	ppm	part per million
in	inch	psia	pound per square inch, absolute
kcal	kilocalorie	psig	pound per square inch, gauge
L	liter	wt %	weight percent
min	minute		

SUPERCRITICAL CO₂ SOLUBILITY OF TiCl₄

By W. K. Tolley¹ and L. S. Tester²

ABSTRACT

The Bureau of Mines is testing supercritical fluids as solvents to selectively extract valuable components from complex matrices. Materials recovered during supercritical fluid extraction are often highly purified. Using laboratory apparatus designed specifically for supercritical fluid research, Bureau researchers have measured the solubility of titanium tetrachloride (TiCl₄) in supercritical, liquid, and gaseous carbon dioxide (CO₂). CO₂, a commonly used supercritical fluid, is inert, inexpensive, and nontoxic. Supercritical CO₂ formed a single phase with TiCl₄ at 45° C and 1,500 psig. When the solution was heated at constant pressure beyond 55° C, TiCl₄ precipitated from the fluid. Results showed that TiCl₄ solubility in supercritical CO₂ is not controlled by the vapor pressure of the solute.

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INTRODUCTION

The Bureau of Mines is investigating the application of supercritical solvent systems for processing minerals and metals. Early reports of solubility in supercritical solvents describe dissolution of inorganic metal salts (1).³ Geologists have shown that minerals may be soluble in supercritical solvents (2). At present, however, supercritical fluids are used almost exclusively by the food and petrochemical industries (3). Except for modifications of the Mond process (4) where supercritical carbon monoxide (CO) was used to produce nickel carbonyl (Ni(CO)₄), no uses of supercritical fluids in extractive metallurgy were found in the literature.

A supercritical fluid is formed when a liquid or vapor is heated and pressurized beyond the critical point. As shown in figure 1, the critical point occurs at a higher temperature and pressure than the boiling point. At the critical point, vapor and liquid phases become indistinguishable and form a single fluid phase with characteristics intermediate between a liquid and a gas. Above the critical point, a liquid phase cannot be produced by compressing the fluid.

Any stable chemical or chemical mixture can be heated under pressure to the supercritical state. Critical temperatures and pressures of chemicals commonly used as

³Italic numbers in parentheses refer to items in the list of references preceding the appendix at the end of this report.

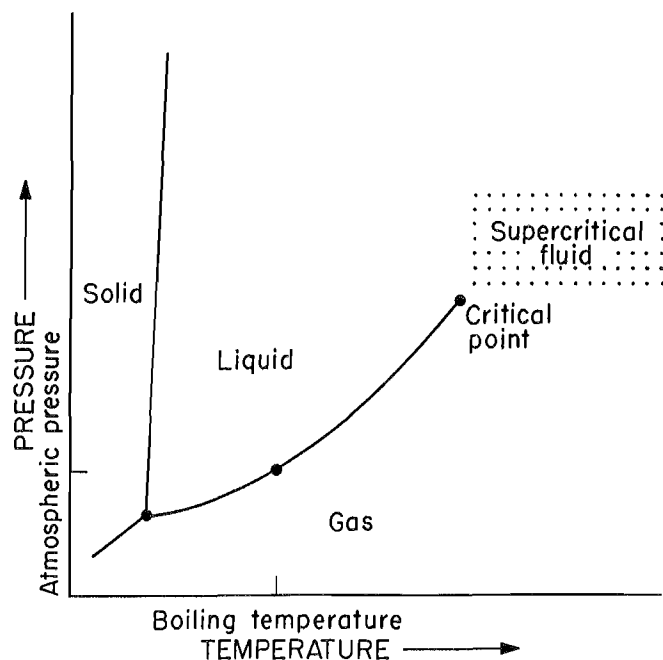


Figure 1.—Phase diagram typical of all chemicals, showing supercritical fluid phase.

TABLE 1.—Physical data for common supercritical solvents

Substance	Boiling point, °C	Critical point	
		Temp, °C	Pressure, psia
Freon-13 (CCl ₂ F ₂)	-81.4	28.8	598
Carbon dioxide (CO ₂) . . .	-78.5	31.1	1,071
Ethane (C ₂ H ₆)	-88.6	32.3	714
Nitrous oxide (N ₂ O)	-89.5	36.5	1,052
Ammonia (NH ₃)	-33.4	132.4	1,636
Sulfur dioxide (SO ₂)	-10	157.2	1,144
Water (H ₂ O)	100	374	3,198

Sources: References 5-6.

supercritical solvents are listed in table 1 (5-6). Note that chemicals with boiling points below -75° C reach the critical state near room temperature. CO₂ is the most commonly used supercritical solvent because it has a low critical point (31.1° C and 1,071 psia) and is chemically stable, nonflammable, nontoxic, and inexpensive.

Much information has been written on supercritical fluid processes. The most notable process involving supercritical fluid extraction is the removal of caffeine from coffee beans using supercritical CO₂ (7). Similar processes have been proposed to recover flavors from vegetable matter (8), chemicals from coal (9-10), and oil from tar sand (11). Available data show the high selectivity of supercritical fluid extraction compared with liquid extractions. For example, vegetable oils extracted with supercritical CO₂ contain less phosphorus and metal than oils recovered by hexane extraction (12). Recent innovations include using supercritical fluids as reactants (13-14) or media for chemical reactions (15).

Supercritical fluid extractions have shown utility in separating substances having differing volatilities (7). Three criteria have been suggested to predict what materials may be suitable for supercritical fluid extraction (16):

1. Hydrocarbons or lipophilic compounds of low molecular weight and polarity are easily extractable with supercritical CO₂;
2. The presence of polar groups renders a compound difficult or impossible to extract with supercritical CO₂, and as a result, sugars, starches, and amino acids are not extracted satisfactorily with supercritical CO₂; and
3. Fractionation of mixtures is possible if components differ in mass, vapor pressure, or polarity.

Some materials that appear to meet the criteria for supercritical fluid extraction are volatile metal chlorides, such as titanium tetrachloride (TiCl₄) (17) and germanium chloride (GeCl₄) (18), and metal carbonyls, such as Ni(CO)₄ and cobalt carbonyl (Co₂(CO)₈).

Of these candidates, TiCl₄ is the most widely used and commercially important material. It is used extensively to

produce titanium dioxide (TiO_2) pigments and titanium metal. It is also used as a catalyst in the manufacture of polymers, notably high-density polyethylene. TiCl_4 is a nonpolar compound that is miscible with hexane and similar hydrocarbon solvents (19). Its boiling point is 136°C , and its critical point has been estimated to be 360°C and 671 psia (20). Because TiCl_4 meets the criteria for supercritical fluid extraction and is commercially important, research was initiated to measure the solubility of TiCl_4 in supercritical fluids.

CO_2 was chosen as the best supercritical solvent for this investigation:

1. CO_2 is chemically stable in contact with TiCl_4 . Thermodynamic data (table 2) indicate that many of the

common supercritical solvents (table 1), including CCl_2F_2 , NH_3 , N_2O , and SO_2 , may react with TiCl_4 and, therefore, are unsuitable.

2. CO_2 is not hazardous. C_2H_6 poses a flammability hazard even though thermodynamics indicate that it would be stable with TiCl_4 .

TABLE 2.—Thermodynamic data for candidate supercritical solvents

Solvent	$\Delta G,^1$ kcal	Solvent	$\Delta G,^1$ kcal
CO_2	93.1	NH_3	-24.1
C_2H_6	84.3	N_2O	-67.4
CCl_2F_2	-10.4	SO_2	-84.3

¹Reaction with 1 mol TiCl_4 at 25°C .

EXPERIMENTAL

EXPERIMENTAL STRATEGY

The flowthrough apparatus used in this study was similar to equipment used by other researchers measuring solubilities in supercritical fluids (21). It is recognized that this experimental method suffers from poor sensitivity due to inherent experimental error (22); thus, small but significant details in the solubility may have gone unnoticed in this investigation. However, sophisticated analytical methods, such as gas chromatography and mass spectrometry, have not been developed to measure the concentration of metal chlorides in high-pressure fluids.

Several checks of the data were included in the experimental scheme. The test sequence was randomized to reduce the effects of possible systematic drift in the operation of the system. Equilibrium solubility was approached from supersaturation as well as from undersaturation of the supercritical stream (23). Several tests were replicated to assure reproducibility. Measurements of known values, such as the vapor pressure of TiCl_4 , were included; accurately measuring known data using the test apparatus provided evidence that test procedures were valid. As a further check, measurements were made using N_2 rather than CO_2 . At ambient pressure, both N_2 and CO_2 are ideal gases and should yield identical results. In contrast, CO_2 at any supercritical temperature and pressure is nearer its critical point than N_2 is at the same conditions; CO_2 , therefore, should have a higher affinity for TiCl_4 (24).

REAGENTS

Special care was taken to use water-free CO_2 in these tests because TiCl_4 is extremely reactive toward water, as are most anhydrous metal chlorides. Coleman Instrument⁴ grade CO_2 (minimum purity of 99.99%), available from various vendors, met the research requirements.

⁴Reference to specific manufacturers or products does not imply endorsement by the Bureau of Mines.

Commercial TiCl_4 was used throughout this investigation. An analysis of the TiCl_4 is provided in table 3.

TABLE 3.—Analysis of TiCl_4 used in solubility determinations

Element	Concentration in TiCl_4 , ppm
Aluminum	17.2
Iron	7.3
Silicon	3.8
Tin	24.7
Vanadium	7.6

EQUIPMENT

When this study was initiated, no suitable supercritical extraction systems were available for TiCl_4 solubility research. Other researchers (22) also have noted the inflexibility of available supercritical extraction apparatus. Therefore, Bureau personnel designed and assembled the specialized laboratory apparatus using available components. Suppliers of these components are listed in table 4. Because the apparatus was specially designed, a detailed description follows.

Basic Laboratory Apparatus

The test apparatus is shown in figure 2. System components included solvent feed, pressure and temperature controllers, extractor vessel(s), and separators for collecting analytical samples. Stock items were purchased from various manufacturers to construct this system.

Cubicles, especially designed for high-pressure testing, housed the supercritical extraction equipment. Remotely operated controls provided additional safety. Air-operated valves actuated remote sampling of the supercritical extract during tests. Manual valves were operated only before and after tests to purge the system.

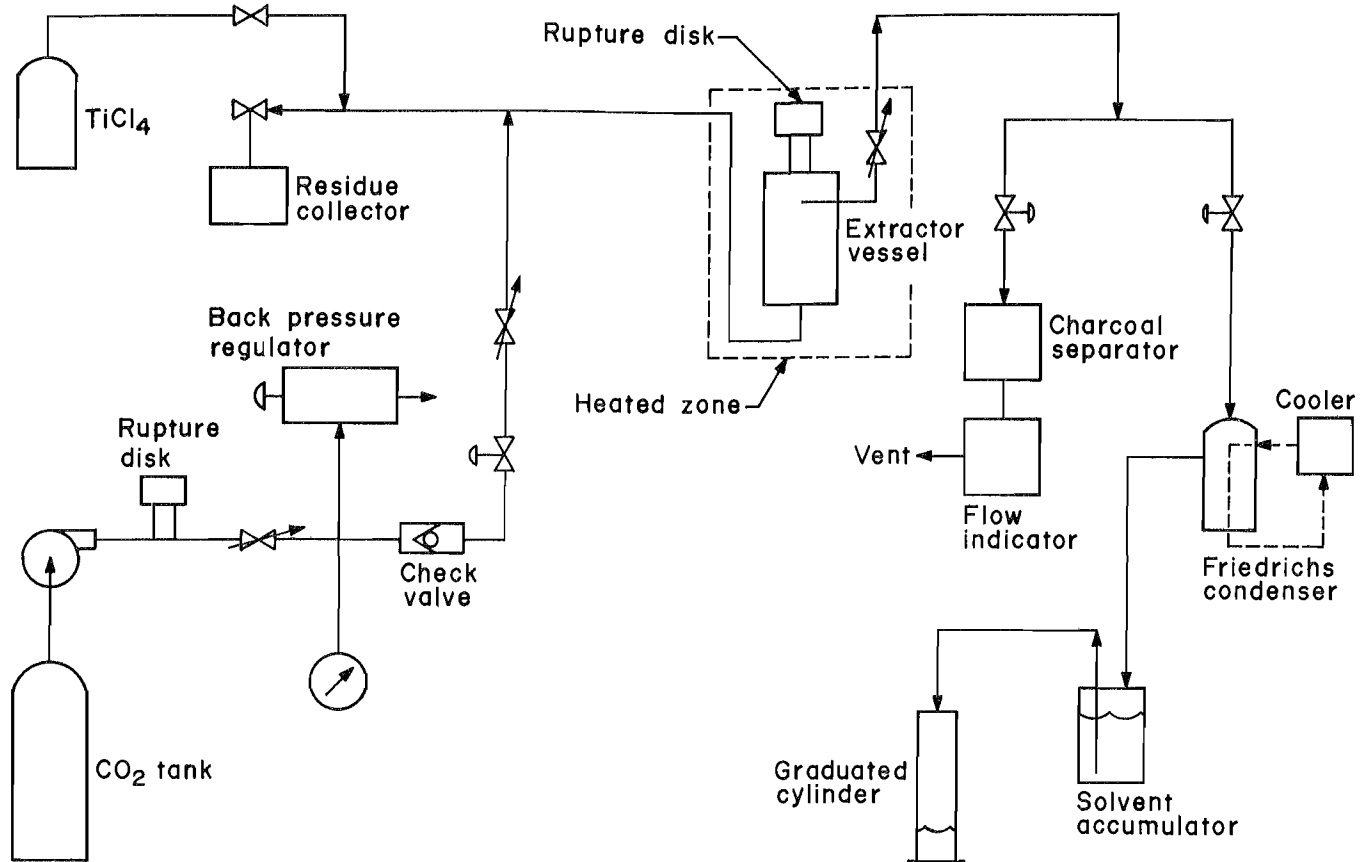


Figure 2.—Standard supercritical fluid test apparatus.

TABLE 4.—Partial list of manufacturers supplying equipment for laboratory-scale supercritical extraction apparatus

Component	Manufacturer or brand name	Component	Manufacturer or brand name
Solvent gas	Local welding gas suppliers. Matheson Gas Co. Scott Specialty Gases.	Gauge	Autoclave Engineers. Heise.
Pump	American Lewa. Eldex. Milton Roy LDC Mlnlpump. Newport Scientific.	Extractor vessel and autoclave	Autoclave Engineers. Newport Scientific. Parr Instrument Co.
Vortex-tube cooler	Vortec Corp.	Valve, tubing	Autoclave Engineers. Heise. Newport Scientific. Parr Instrument Co. Whitely Co.
Back-pressure regulator	Haskel Supply Co. Tescom Corp.	Constant-temperature bath	Ruska Instrument Corp. Techne Corp.

The test apparatus was constructed primarily of AISI Type 316 stainless steel with minor amounts of Teflon fluorocarbon polymer. Seamless 1/4- or 1/16-in-OD stainless steel tubing was used where high strength was required. Teflon polymer tubing of similar diameters was used elsewhere to reduce the possibility of corrosion. Tubing was connected with swaged fittings capable of handling

pressures up to 6,000 psig and temperatures up to 350° C. To prevent leaks, Teflon polymer sealing tape was wrapped around the tubing and the ferrule in the fittings; this was especially helpful where fittings deformed through frequent disassembly. Valves were fabricated from 316 stainless steel and packed with Teflon polymer.

Solvent Feed System

CO₂ was the primary solvent used throughout this investigation. The CO₂ was supplied under pressure in compressed-gas cylinders and was pumped as a liquid through an eductor tube in the cylinder. As a precaution, the solvent was filtered through fritted metal elements at the pump inlet. A liquid chromatography pump fed liquefied solvent to the supercritical extraction apparatus. The pump head was cooled to prevent solvent vaporization due to the heat of compression. Chilled air from a vortex-tube cooler provided satisfactory cooling. In a vortex tube, compressed air is directed into a cyclone, yielding cold air in the low-pressure vortex. Pump efficiency was optimum when the vortex cooler held the temperature below approximately -10° C.

Pressure and Temperature Controls

In the Bureau apparatus, a pressure gauge to indicate system pressure was connected to the pump outlet. A back pressure regulator was connected between the pump and the extractor vessel to release gas or liquid when system pressure exceeded an adjustable setting. A reversible motor adjusted this pressure setting to allow remote operation of the system. The back pressure regulator was able to maintain the pressure within 50 psig of the desired setting. To prevent solidification of expanding solvent during pressure releases, the back-pressure regulator was wrapped with heating tape.

A thermocouple monitored the internal temperature of the supercritical apparatus. A fluidized sand bath provided uniform heating of the extractor vessel, feed lines, and exhaust lines. The temperature was maintained within 1° C of the setting during solubility determinations. Temperature uniformity throughout the system was very important to prevent premature precipitation of the TiCl₄.

Extractor Vessel

The extractor vessel, which was a 1-in-OD by 10-in length of 316 stainless steel tubing, held the TiCl₄ feed sample; working volume of this vessel was approximately 70 mL. A rupture disk located immediately above the extractor vessel was connected through 9/16-in-OD tubing, which was larger than other system piping and allowed pressure surges to rupture the disk before sensitive components could be damaged.

Solvent entered at the bottom of the extractor vessel and dissolved solute while bubbling upward through the test sample. Stainless steel wire mesh placed inside the extractor dispersed the CO₂ bubbles to improve contact with the liquid test sample. The supercritical stream containing solubilized TiCl₄ exited through the top of the extractor.

Pressure Reduction, Sampling, and Solvent Measurement

After leaving the extractor vessel, the supercritical stream was depressurized by passing through a needle valve on the extractor vessel outlet.⁵ The needle valve was immersed in the fluidized sand bath to maintain a constant temperature in the fluid phase and to prevent freezing of the expanding fluid. During depressurization, the CO₂ pressure dropped to ambient, causing solute to precipitate from the expanding gas. The liquid precipitate was captured in 100- to 300-mL glass separators. A Friedrichs condenser proved to be the best separator for sampling; the condenser was chilled to assure complete condensation of the TiCl₄. During equilibration or venting of the system, an Erlenmeyer flask filled with charcoal acted as a separator.

Moisture was excluded from the system by using high-purity CO₂ as the solvent and by keeping the system under slight pressure whenever possible. Dry charcoal scrubbers on all vent lines from the system acted to absorb corrosive fumes and to prevent inadvertent infiltration of moist air.

PROCEDURES

Standard Test Procedure

Heating the extractor was usually the first step in a run because of difficulty in attaining thermal equilibrium. Heating was monitored carefully because cooling the apparatus following an inadvertent temperature excursion was particularly difficult. The exact procedure for heating the apparatus depended on the desired operating temperature. For temperatures below 60° C, the system was preheated before TiCl₄ was put into the extractor. At higher temperatures, the TiCl₄ vapor pressure was enough to interfere with siphoning of the sample into the extractor vessel, so the system was filled before the extractor was fully heated.

TiCl₄ is hygroscopic; therefore, care was taken to prevent water or moisture from reaching the feed material or the interior of the apparatus. Before each test, 50 mL TiCl₄ was siphoned by vacuum from a closed 500-mL graduated cylinder into the extractor vessel. This arrangement allowed many tests to be run without opening or otherwise contaminating the system. Once the sample was in place, solvent flow was started immediately to maintain moisture-free conditions. When required, the temperature then was raised to the target setting and allowed to stabilize before testing proceeded further.

⁵When operating at pressures above the CO₂ tank pressure, the needle valve between the extractor vessel and the air-operated valves was used to control flow; the other needle valves were opened to full flow. When operating at pressures lower than the CO₂ tank pressure, pressure and flow were controlled through a combination of all three needle valves.

Once the sample was in place and at temperature, pressurizing was begun. After the system stabilized at the desired operating conditions, the supercritical extract was vented for approximately 30 min to ensure stable operation before analysis started. The solvent flow was adjusted as needed during this period to maintain the desired rate.

To analyze the supercritical stream, the flow of extract was redirected from the vent to the sampling section of the apparatus by activating the appropriate air-operated valves. The extract at this point was at ambient pressure. Extract in the sampler first entered the separator, which was chilled to approximately -15°C to obtain complete condensation of the TiCl_4 from the CO_2 gas. The amount of TiCl_4 in the extract was determined by weighing the separator along with the TiCl_4 condensate after each test. The CO_2 content of the extract was measured by capturing the CO_2 gas in a stoppered bottle as it left the separator. Approximately 2 L of solute-free gas was captured over a 30- to 60-min period. Gas entering the bottle displaced an equal volume of water, which was measured easily. Solubility measurements were terminated at this point. After each run, undissolved TiCl_4 was drained from the extractor vessel, weighed, and discarded.

Nonstandard Test Procedures

Test procedures were altered for specific reasons in several of the tests. These altered procedures are described individually.

Approaching Equilibrium From Supersaturation

In the standard test procedure, solute-free CO_2 solvent entered the equilibration vessel; thus, equilibrium was approached from the starting point of pure components. However, true equilibrium is independent of any starting point (23); hence, tests were run in which equilibrium was approached from the point of excess solute in the supercritical stream. To do this, two extractor vessels were placed in series as depicted in figure 3. The temperature in the first vessel was maintained at 32°C . The temperature in the second vessel was 55° , 75° , or 95°C , which was expected to reduce the TiCl_4 solubility. The pressure was controlled at the inlet to the first vessel as was done in standard tests. Because of the pressure drop in transferring fluid from the first to the second vessel, the pressure was slightly lower in the second vessel, where analysis

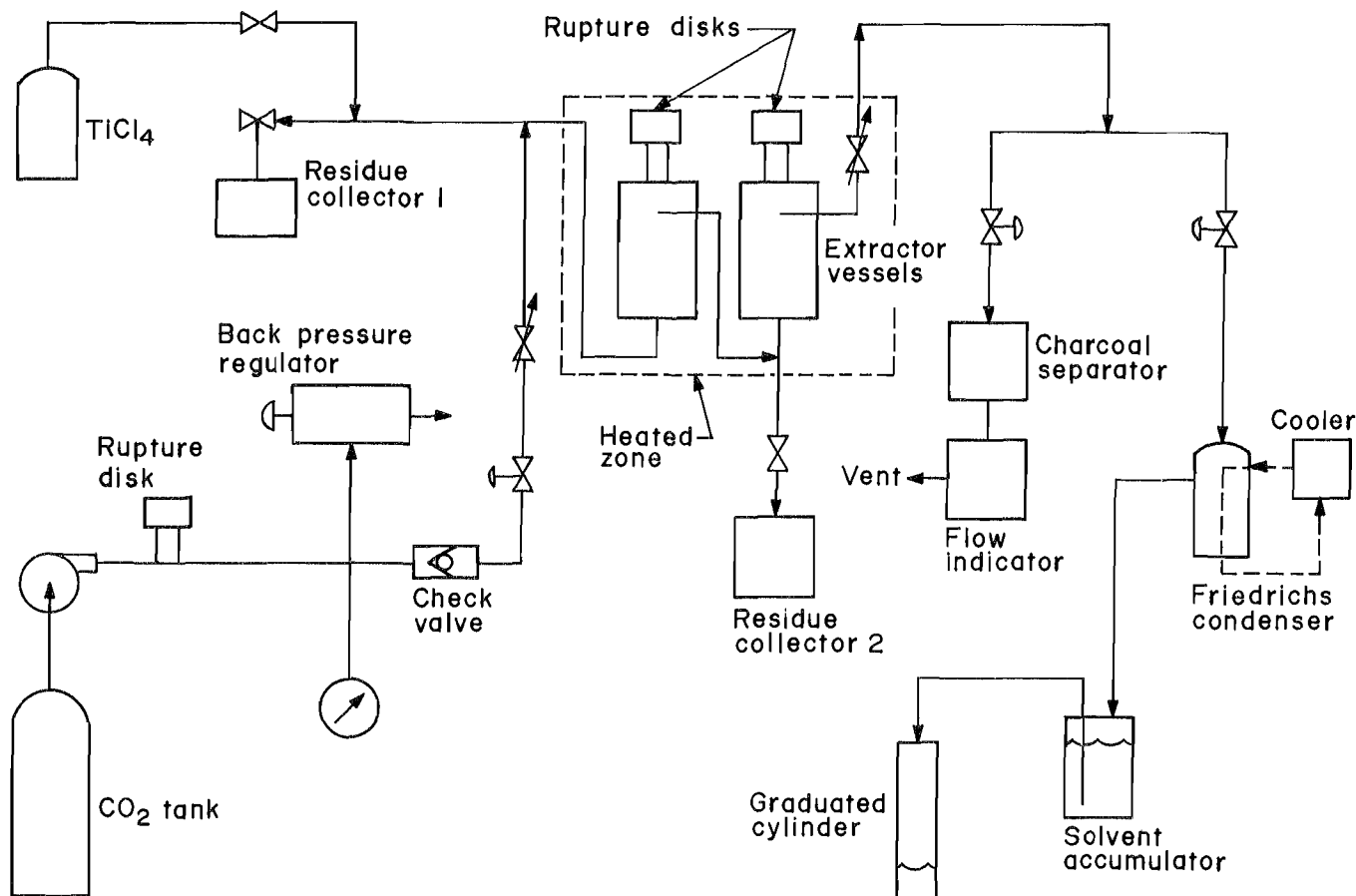


Figure 3.—Dual-stage supercritical fluid test apparatus.

of the fluid occurred. The sampling procedure for these tests was identical to the standard procedure. After each run, the vessels were drained into separate collectors.

Larger Sample Size

Solubility is an intensive property and is, therefore, unaffected by the amount of sample used to measure it.

To assure that sample size of the extract was not biasing solubility determinations, larger than standard samples of extract were collected. Procedures for these tests were identical to standard tests except that 8 L of depressurized supercritical extract was analyzed over a period of approximately 200 min rather than the standard 2 L analyzed over a 40-min period.

RESULTS AND DISCUSSION

TiCl₄ SOLUBILITY

The stated objective of the research was to determine the solubility of TiCl₄ in supercritical CO₂. Equilibrium solubility necessarily assumes that multiple, immiscible phases are present in the system of interest. However, TiCl₄ and CO₂ were found to be totally miscible at many combinations of temperature and pressure. At such conditions, solubility is infinite. The system is stable as a single liquid phase. Low temperature and high pressure favor formation of a stable liquid phase. A complete tabulation of the data is reported in table A-1 of the appendix.

Effect of CO₂ Flow Rate

The methods used in this study are similar to those used by other researchers to measure solubilities in supercritical fluids. To obtain accurate solubility data in a flow apparatus, it is necessary to maintain low solvent flow rates that do not disturb the equilibrium (21). The experimental error was smallest when flow rate during sampling did not exceed 4 L of depressurized extract per hour.

TiCl₄ Behavior in Gaseous CO₂

As a check to assure reliable data, measurements of known data were run using this apparatus. The vapor pressure of TiCl₄ is known accurately (25) and was chosen as a standard to test the operation of the apparatus. Based on a total system pressure of 1 atm, the concentration of TiCl₄ in a saturated gas was calculated and plotted in figure 4. Measurements of the TiCl₄ vapor pressure made with the test apparatus also are plotted. The data show typical vapor pressure behavior; TiCl₄ concentration in the gas increases with increasing temperature, reaching a high of 67 wt % in the CO₂ at 95° C. These data suggest that CO₂ may act as an inert purge gas to remove TiCl₄ from the apparatus.

To reinforce these results, measurements were repeated using N₂ in place of CO₂, as shown in figure 4. These data also agree well with known TiCl₄ vapor pressure. Because measurements using the test equipment agree with known

data, it is believed that solubilities measured in supercritical CO₂ adequately represent TiCl₄ behavior in the supercritical fluid.

TiCl₄ Behavior in Supercritical CO₂

Data collected during this investigation show that TiCl₄ is highly soluble in supercritical CO₂. Standard deviation of the TiCl₄ solubility, reported as weight percentage, was determined to be 5.3 for these tests. This value is consistent with the experimental error reported by others using a similar system (22).

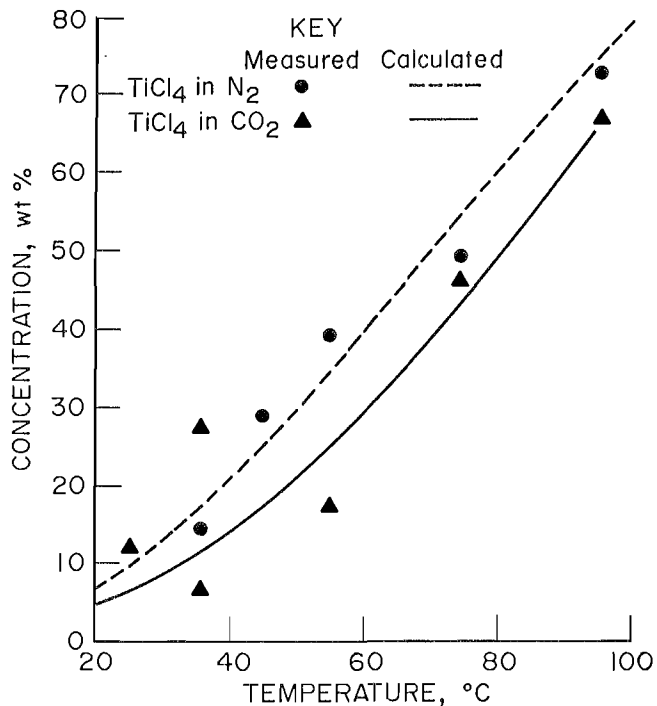


Figure 4.—TiCl₄ extraction with gaseous CO₂ and N₂ at 1 atm system pressure. Solid and dashed lines represent expected results calculated from vapor pressure data.

Solubility of TiCl_4 in CO_2 is plotted against temperature and pressure in figure 5A. The vertical axis represents TiCl_4 solubility as weight percentage in the supercritical or the vapor phase. Lines along the solubility surface connect points of constant temperature (isotherms) or constant pressure (isobars). Along any isotherm, solubility initially decreases as the pressure rises from ambient to about 700 psig. As the pressure increases above this value, solubility increases. At 45° C, the solubility rises steeply with increasing pressure between about 700 and 1,500 psig (approximately 400 psig below to 400 psig above the critical pressure). At approximately 1,500 psig, supercritical CO_2 becomes totally miscible with liquid TiCl_4 . The system becomes stable as a single liquid phase and is not affected by increased pressure.

Temperature also strongly affects solubility, as depicted in figure 5B. At 1,500 psig, TiCl_4 and CO_2 form a single liquid phase below 50° C. Isobaric heating from this temperature caused separation into distinct liquid and vapor phases. Along the 2,100 psig isobar, only a liquid phase was observed up to 95° C.

Approaching Equilibrium From Supersaturation

As described earlier in this report, the standard test method approached equilibrium from undersaturation. To confirm the observed relationship between heating and TiCl_4 solubility, tests were run in which equilibrium was approached from the point of supersaturation. This was

accomplished by using the two-vessel apparatus; CO_2 was mixed with TiCl_4 at 32° in the first vessel, and the mixture was isobarically heated in the second vessel. The data from these tests are reported in table 5. It is evident that solubility at 1,500 psig decreases substantially when the temperature is raised above 55° C. Consistent reduction of TiCl_4 solubility upon heating, whether approached from undersaturation or supersaturation, further confirms that this represents equilibrium behavior. Although lower TiCl_4 concentrations were measured in the supersaturation tests, the conclusion that TiCl_4 concentration drops during isobaric heating still appears valid.

TABLE 5.—Effect of isobaric heating on TiCl_4 solubility at 1,500 psig, weight percent

Temperature, °C	1 vessel	2 vessel
55	63.0	51.8
75	41	18.8
95	23.8	17.5

Larger Sample Size

In selected tests, the analytical sample size was increased by a factor of 4 to ensure that it was not influencing the data. At equilibrium conditions, sample size should not affect the ratio of TiCl_4 solute to CO_2 solvent in the extract. Table 6 compares the TiCl_4 content of the extract for the two sample sizes at two temperatures. The concentration of TiCl_4 in the extract appeared unaffected by sample size in tests at 55° C; at 95° C,

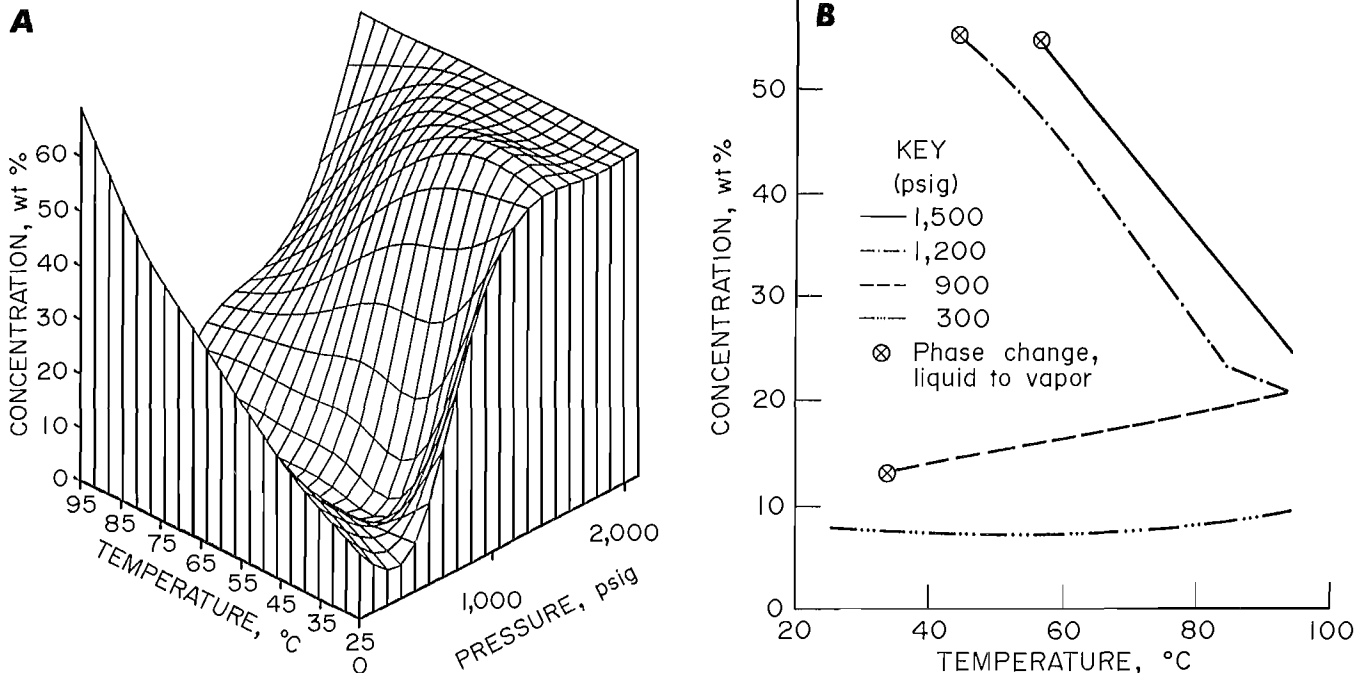


Figure 5.— TiCl_4 solubility in CO_2 . A, 3-D plot of data; B, selected solubility isobars showing reduced TiCl_4 solubility in supercritical CO_2 caused by heating.

however, TiCl_4 concentration in the extract was *lower* in the larger samples. No rationale has explained this discrepancy, but the data again show that TiCl_4 solubility is much lower at 95° C than at 55° C.

TABLE 6.—Comparison of TiCl_4 solubilities determined from different analytical sample sizes,¹ weight percent

Temperature, °C	Sample size, L	
	2	8
55	59.3	57.9
	66.6	65.3
95	23.0	12.8
	24.7	10.7

¹Conditions: 1,500 psig.

COMPARISONS WITH OTHER SUPERCRITICAL FLUID SYSTEMS

The data illustrated in figure 5 typify solute behavior observed by researchers studying other solutes in supercritical fluids. For example, solubility of oleic acid in supercritical CO_2 (26) at 3,000 psig, although much lower than TiCl_4 , *decreased as the temperature rose* from 40° to 120° C; similarly, TiCl_4 solubility at 1,500 psig *decreased upon heating* of the supercritical fluid above 55° C. Solubility of benzoic acid and 2,3-dimethylnaphthalene (DMN) in CO_2 (21) dropped sharply as the pressure increased from ambient to about 300 psig, then rose between about 600 and 1,800 psig; increasing pressure beyond 1,800 psig had little effect on the solubilities. The TiCl_4 behaved similarly, as can be seen in figure 5A. Thus, TiCl_4 in supercritical CO_2 behaves much like other solutes, which should aid in designing a system to recover TiCl_4 using supercritical CO_2 . It is also clear that TiCl_4 solubility in supercritical CO_2 is not controlled by vapor pressure.

EQUIPMENT OPERATION

A collateral objective of this study was to gain experience in handling metal chlorides during supercritical fluid extraction. The corrosive nature of TiCl_4 was especially troublesome in analyzing the supercritical extract. Initially, TiCl_4 was scrubbed from the CO_2 gas with dilute hydrochloric acid. This was advantageous because TiCl_4 was completely soluble in the acid while CO_2 was completely insoluble. However, it was impossible to keep moisture out of process lines using aqueous scrubbers. Another unsatisfactory analytical method was to adsorb the TiCl_4 with activated charcoal. This effectively removed TiCl_4 from the vapor but yielded poor analyses because CO_2 also adsorbed on the charcoal. Ultimately, the supercritical extract was analyzed by chilling the separator vessel to condense TiCl_4 out of the gas stream. This required great care because TiCl_4 is highly volatile; hence, the separator had to be maintained at temperatures below -10° C. Liquid coolant caused problems when Erlenmeyer flasks were used as separators by leaking past seals to react violently

with TiCl_4 . A workable solution proved to be using a Friedrichs condenser as the separator. The condenser was chilled either with air from the vortex cooler or with coolant from a refrigerated bath. Coolant passed through the vapor side of the condenser, and depressurized extract passed through the liquid side of the condenser. The spiral shape of the condenser walls aided cooling and coalescence of the condensing TiCl_4 .

Durability of materials in contact with corrosive TiCl_4 was monitored throughout this research. Corrosion of the stainless steel components was insignificant as long as water was excluded from the system. Neither visual inspection nor scanning electron microscopy (SEM) examination revealed signs of corrosion inside the system after operating for approximately 1,000 h. Teflon polymer materials also appeared unaffected by contact with supercritical mixtures of CO_2 and TiCl_4 . Natural cork was stable in contact with TiCl_4 vapors but was too porous to confine pressurized fluids. Rubber seals and stoppers cracked after contact with the supercritical solutions and were replaced with Teflon polymer. Dry test meters were not used to monitor CO_2 flow because of the corrosion potential and because flow rates were small.

As in all heterogeneous extraction systems, mass transfer affects the performance of the apparatus. Adding wire mesh diffusers in the extractor vessel was beneficial in these tests by dispersing the CO_2 into the liquid TiCl_4 . Further research on the effects of mass transfer in supercritical fluid extraction appears warranted.

As was seen in figure 5, TiCl_4 solubility in supercritical CO_2 is very sensitive to temperature and pressure. In these laboratory tests, a fluidized sand bath heater was most effective for maintaining temperature uniformity throughout the supercritical extraction system. Heating tapes or band heaters did not provide adequately uniform temperatures.

POTENTIAL APPLICATIONS

TiCl_4 solubilities measured during this investigation are relevant to processes for recovering or purifying TiCl_4 . One approach to recovering TiCl_4 is to heat it in the presence of a purge gas at ambient pressure. Such a procedure avoids the capital costs for pressure equipment and the operating costs of compressing the solvent to supercritical pressures. However, literature references indicate that this method is unsatisfactory for adequately separating TiCl_4 from other metal chlorides (27).

A simple supercritical extraction process for recovering TiCl_4 would be to dissolve the TiCl_4 in supercritical CO_2 at 1,500 psig near 50° C. TiCl_4 could be recovered in a separate chamber by isobaric heating to approximately 95° C. Heating and cooling over this temperature range is relatively inexpensive, and costly pressure swings would be avoided. Two potential applications of such a process are apparent. The first is purification of TiCl_4 intermediate,

used to produce ceramics, titanium metal, or TiO_2 pigments. If supercritical fluid extraction proves to be highly selective and cost effective, it could replace distillation to purify the TiCl_4 . The second potential application is removing TiCl_4 from other materials. For example, Bureau personnel determined that TiCl_4 was one of the most troublesome impurities in an aluminum chloride (AlCl_3) product generated by carbochlorination of kaolin clay (27-28). About 10% of the chlorinated product is TiCl_4 , but adequate TiCl_4 removal has not been accomplished in

practice. If an effective separation of TiCl_4 and AlCl_3 were developed, domestic kaolin clays could become an economically viable source of aluminum to replace imported aluminum ores.

Ultimately, supercritical fluid extraction may have application in the production of many metals. Metal carbonyls and GeCl_4 are other candidate materials for supercritical fluid extraction. As a greater understanding of supercritical fluid extraction develops, other applications may become obvious.

SUMMARY

TiCl_4 proved to be highly soluble in supercritical CO_2 . Solubility varies greatly with the temperature and pressure of the CO_2 solvent. Supercritical CO_2 is totally miscible with TiCl_4 near 1,500 psig between 32° and 50° C. Isobaric heating of the supercritical solution above 55° C caused precipitation of TiCl_4 from the solution. This reduced solubility may be ascribed to decreased density of the supercritical solvent caused by heating. The effect of higher pressure was inconsequential in this temperature

range but was significant at higher temperatures (75° to 95° C).

The relationship between temperature and solubility in supercritical CO_2 demonstrates that solubility is not controlled by the vapor pressure of the solute. The data collected demonstrate that vapor pressure of TiCl_4 increases steadily with temperature while TiCl_4 solubility in the supercritical phase decreases with increased temperature.

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APPENDIX

TABLE A-1.—TiCl₄ solubility in CO₂

Pressure, psig	Temperature, °C	TiCl ₄ solubility, wt %	Pressure, psig	Temperature, °C	TiCl ₄ solubility, wt %
0	25	12.4	900	32	SLP
	36	7.0		35	13.4
	36	27.7		55	15.9
	56	17.2		55	23.5
	96	66.8		75	15.5
300	32	7.9		75	21.9
	55	7.1		75	7.0
	95	9.5		95	19.5
550	42	12.1		95	21.6
	112	31.2	1,000	33	SLP
600	35	13.4	1,200	32	SLP
	42	12.4		35	SLP
	52	12.5		46	SLP
	93	13.9		55	49.0
650	115	30.9		76	27.4
700	25	38.5		95	12.8
	37	7.9		95	19.1
	115	26.7	1,500	55	SLP
750	33	5.7		74	41.0
	35	8.5		95	24.7
	57	13.5		95	23.0
800	32	14.6	1,800	55	SLP
	52	9.8		94	26.8
	95	18.5	2,000	51	SLP
850	76	17.5		95	51.5
900	26	SLP	2,100	95	SLP

SLP Single liquid phase present.