Solubility of Solid Methylene Chloride and 1,1,1-Trichloroethane in Fluid Oxygen[†]

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The solubilities of solid methylene chloride and solid 1,1,1-trichloroethane in fluid oxygen have been measured using a single-pass continuous flow apparatus. Oxygen, at supercritical pressures, is passed through an equilibration column immersed in a controlled-temperature bath. Both open tubing and tubing packed with solute-coated firebrick are used as equilibration columns. The saturated stream is returned to ambient conditions and analyzed for solute concentration by a gas chromatograph with a flame ionization detector. Methylene chloride solubilities ranged from 4.8 ppb at 94.3 K to 47.6 ppm at 155.4 K and 1,1,1-trichloroethane from 19.2 ppb at 94.3 K to 38.8 ppm at 194.6 K. Pressures ranged from 55.2 to 100 atm. At a given temperature, the concentration was found to be a linear function of the solvent pressure.

Introduction

Methylene chloride and 1,1,1-trichloroethane have been used as solvents to clean equipment to be used in oxygen service. If significant quantities of these potential fuels remained in the equipment after the cleaning process hazardous conditions could exist. Knowledge of the solubility limit corresponding to the temperature of a storage vessel from which liquid samples are taken allows one to evaluate the potential hazard. If the concentration of the chlorinated hydrocarbon is below the solubility limit one can assume there is no solid phase in the vessel, whereas if the concentration is equal to the solubility limit one can conservatively assume that the solid phase is present in the vessel.

The single-pass, continuous flow technique with the solvent above its critical pressure, has been shown (*1*, *2*) to be an effective method for obtaining solubility data. Data for the above systems were obtained by either of two experimental techniques. One method is to pass pure oxygen through a column packed with solute-coated firebrick. The other method is to pass supersaturated oxygen through an open tube column allowing the excess solute to deposit in this column. Pure oxygen can then be passed through this column and dissolve the previously deposited solute.

Experimental Section

Materials and Sample Analysis. Ultrapure carrier grade oxygen (99.994%) obtained from Air Products and Chemicals, Inc., was used as the solvent material. Fisher certified ACS methylene chloride and Target reagent grade 1,1,1-trichloroethane were used as solute materials. These materials were used without further purification. The relatively small amounts of impurities in the methylene chloride tended to leach out within a few hours after start up time. The reagent grade 1,1,1-trichloroethane contained about 2% impurities and complete flushing of all the impurities from the solute-coated firebrick column was not accomplished. The impurities do not appear to influence the solubility of the major component but can affect the integrated peak areas since a complete chromatographic separation of all the components was not obtained.

Solute concentrations were determined with a gas chromatograph and a hydrogen flame ionization detector (FID). A 5-cm^3 sample loop and a 1.8-m (4.8 mm o.d., 3.8 mm i.d. stainless steel) column packed with 7.5% Carbowax 400 on Chromosorb T (40/60 mesh) were used for the early methylene chloride work in the concentration range above 1 molar ppm. The column temperature was 50 °C with a 60-cm^3/min helium carrier flow rate. A 10-cm^3 sample loop and a 1.8-m (6.4 mm o.d., 5.4 mm i.d. stainless steel) column packed with Tenax-GC (60/80 mesh) were used for methylene chloride over the entire concentration range in later work on the system. A column temperature of 115 °C with 60 cm^3/min of helium carrier was used. A 1.5-m column packed with molecular sieve adsorbent (MS 5A, 40/50 mesh) and cooled in a liquid-nitrogen bath was inserted in the helium carrier stream to ensure against trace quantities of hydrocarbons appearing in the carrier stream. A 10-cm^3 sample loop and a 1.5-m (4.8 mm o.d., 3.8 mm i.d. stainless steel) column packed with 8.6% SP-2100 on Chromosorb T (40/60 mesh) followed by a 1.8-m (6.4 mm o.d., 5.4 mm i.d. stainless steel) column with the same packing material were used for all the 1,1,1-trichloroethane work. Atmospheric pressure samples were automatically injected at preselected intervals of 6–15 min. Sample peak areas were measured with an Autolabs System IV computing integrator and compared to peak areas from gas mixtures of known compositions. A 15.2-molar ppm methylene chloride standard was obtained by careful blending and compared to a 1.176% gravimetric standard via a 508-molar ppm gas blend. A 34.0-ppm 1,1,1-trichloroethane gas standard was obtained by direct mass determinations in a 16.4-L lightweight stainless steel cylinder.

Single-Pass Continuous-Flow Apparatus. The basic apparatus has been described previously (*1*). The entire system is assembled from standard copper or stainless steel tubing, metal valves, and commercially available mechanical fittings. The section of coiled tubing which serves as the equilibration column is immersed in a temperature-regulated bath. Copper tubing packed with solute-coated firebrick was used for the methylene chloride work and the initial 1,1,1-trichloroethane work. Column lengths were 2.4 m (6.3 mm o.d., 3.9 mm i.d.) packed with about 24 g of coated firebrick (30/60 mesh), 42% by weight solute. A coiled 2.4 m length of open copper tubing (3.2 mm o.d., 1.6 mm i.d.) preceded the equilibration column in the bath. The reducing union which connected the column to the stainless steel exit line (80 cm, 0.165 mm i.d.) contained a disk of sintered stainless steel (10 μ). The copper sheathed exit line and the commercial needle valve were wrapped with a heat tape. Elimination of all dead-ended sections in the sampling system was found to be essential as they can be persistent sources of contamination when low concentrations are encountered.

In an attempt to resolve later sample concentration variations which resulted from changes in the overall flow rate through the system, the 1,1,1-trichloroethane-packed column was placed in a solid CO_2–Freon-11 bath and a 3-m (3.2 mm o.d., 2.7 mm i.d.) open stainless steel equilibration column was installed in

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Table I. Experimental Results: Oxygen-Methylene Chloride

Temp, K	Pressure, atm	x_{exptl},[a] molar ppm	No. of samples	Rel. error,[b] %	$x_{\text{sat.}}$, molar ppm
155.4	69.0	47.6	11	0.17	
155.4	55.2	32.3	10	0.38	
149.8	68.9	36.3	9	0.17	
149.8	55.3	31.2	12	0.26	
149.8	54.5	32.4[c]	11	0.45	26.0
144.3	54.5	23.1[c]	5	0.27	
141.5	69.0	18.5	12	0.25	
141.5	55.4	17.2	11	0.31	14.7
138.7	68.9	13.6	5	0.36	
138.7	68.6	13.7	11	0.28	
138.7	61.8	13.6	17	0.48	
138.7	55.5	14.5[c]	6	0.12	
138.7	55.2	13.9	5	0.23	
133.2	68.8	8.32	4	0.34	
133.2	55.5	8.37[c]	5	0.22	
133.2	55.2	7.94	8	0.42	6.96
132.0	55.5	7.40[c]	9	0.25	
127.6	68.8	4.36	8	0.61	
127.6	55.5	4.43[c]	6	0.16	
127.6	55.3	4.24	7	1.08	3.88
122.0	55.5	2.18[c]	5	0.24	
120.9	55.5	1.86[c]	6	0.40	
120.3	69.1	1.64	12	2.07	
120.3	55.5	1.64	10	2.37	1.64
116.5	69.0	0.966	12	2.28	
116.5	55.5	0.978[c]	7	0.81	
116.5	55.2	0.924	9	1.53	0.781
110.9	55.5	0.397[c]	6	1.10	
105.4	55.5	0.144[c]	25	2.51	
99.8	55.5	0.0421[c]	45	9.83	
99.8	55.5	0.0439[c]	10	7.26	
99.8	55.5	0.0404	6	9.12	
97.6	55.5	0.0249[c]	7	6.91	
97.6	55.5	0.0244[c]	12	16.6	
94.3	55.5	0.0048[c]	8	27.8	

[a] Molar ppm = 10^6 mole fraction. [b] See Table II, footnote *b*. [c] Data obtained with 10-cm^3 sample loop and Tenax-GC packed separation column.

Table II. Experimental Results: Oxygen-1,1,1-Trichloroethane

Temp, K	Pressure, atm	x_{exptl},[a] molar ppm	No. of samples	Rel. error,[b] %	$x_{\text{sat.}}$, molar ppm
194.6	82.3	22.4	6	0.88	
194.6	68.7	13.3	6	0.49	
194.6	55.6	8.42	4	0.66	
194.3	96.4	38.8	3	0.03	
190.9	95.9	32.9	4	0.25	
190.9	83.8	18.5	6	0.18	
190.9	83.0	17.7	4	0.08	
190.9	69.7	9.57	8	0.56	
188.7	96.3	29.6	3	0.14	
188.7	82.7	15.1	4	0.34	
188.7	68.9	7.60	7	0.53	
183.2	96.3	26.2	5	0.21	
183.2	82.7	11.7	4	0.39	
183.2	69.3	5.06	5	0.46	
183.2	68.9	4.98	11	1.09	
180.0	100.0	28.3	5	0.11	
180.0	90.0	17.1	7	0.19	
180.0	80.0	8.50	4	0.23	
180.0	70.0	4.28	4	0.03	
177.6	96.6	27.1	5	0.22	
177.6	82.6	10.4	13	0.45	
177.6	69.2	3.49	5	0.64	
177.6	69.2	3.56	5	0.61	
174.3	69.1	3.17	6	0.17	
172.0	96.4	22.2	5	0.58	
172.0	69.2	3.12	3	0.10	
168.7	69.2	3.59	10	0.34	
166.0	96.3	34.5	17	0.07	
164.0	100.0	36.9	5	0.12	
164.0	96.3	34.0	7	0.15	
164.0	70.0	8.22	7	0.44	
155.4	82.7	22.8	5	0.97	
155.4	75.9	20.3	2	0.68	
155.4	69.1	17.6	3	0.26	
152.0	75.9	18.1	12	0.55	
152.0	69.1	16.7	10	0.42	
152.0	62.3	15.7	6	0.73	12.6
144.3	69.1	11.2	20	0.87	
140.0	100.0	9.69	5	0.21	
140.0	70.0	8.36	11	0.36	6.48
138.0	100.0	8.22	6	0.21	
138.0	100.0	8.15	6	0.17	
138.0	90.0	7.88	6	0.17	
138.0	80.0	7.55	7	0.15	
138.0	70.0	7.17	11	0.28	5.69
134.0	100.0	5.661	8	0.07	
134.0	90.0	5.496	8	0.09	
134.0	80.0	5.282	10	0.12	
134.0	70.0	5.084	8	0.10	4.13
133.2	96.7	5.22	5	0.25	
133.2	83.0	5.02	7	0.34	
133.2	69.1	4.73	5	0.12	
133.2	69.1	4.79	4	0.11	3.94
130.0	100.0	3.797	6	0.10	
130.0	90.0	3.680	7	0.09	
130.0	80.0	3.581	5	0.10	
130.0	70.0	3.463	6	0.18	2.88
127.6	69.1	2.70	6	0.04	
122.0	69.1	1.43	5	0.13	
120.0	100.0	1.193	8	0.33	
120.0	100.0	1.183	5	0.26	
120.0	90.0	1.162	6	0.15	
120.0	80.0	1.145	5	0.12	
120.0	70.0	1.118	5	0.21	0.982
116.5	69.2	0.712	13	0.38	
110.0	100.0	0.344	5	0.45	
110.0	90.0	0.316	4	0.68	
110.0	80.0	0.308	25	0.89	
110.0	70.0	0.295	6	0.95	0.192
100.0	100.0	0.0559	10	2.22	
100.0	70.0	0.0527	9	3.13	0.0455
94.0	100.0	0.0192	9	6.98	

[a] Molar ppm = 10^6 mole fraction. [b] Relative error = $\{[\Sigma(x_i - \bar{x})^2]^{1/2}/\bar{x}N\} \times 100$ where N = number of samples at a given temperature, x_i = experimental value (area counts), and $\bar{x} = (\Sigma x_i)/N$.

the regulated bath. Provisions were also made to by-pass the packed column (saturator). The flow rate induced variations were later found to be the result of chemical reactions in the heated sample line but the open tube measurements did provide confirmation of the data obtained with the packed column.

An unexpected benefit of the open tube was the disappearance of all detectable impurities when dissolving predeposited solute into the oxygen stream. The impurities which persistently eluted from the packed 1,1,1-trichloroethane column appeared to pass directly through the open equilibration column. When the saturator was by-passed the pure oxygen quickly swept the impurity-containing solution from the column and a relatively "clean" chromatogram was obtained.

Cooling for the temperature bath was provided by liquid nitrogen as described previously (*2*). The bath temperature was measured with a platinum resistance thermometer (Leeds and Northrup 8164) calibrated by NSB according to the International Practical Temperature Scale of 1968. Thermometer resistance was measured with a Mueller bridge (Leeds and Northrup Model G-2). System pressures were measured with 3000-psi (20.6 MPa) Heise-Bourdon gauges.

Results

Methylene chloride data are given in Table I and 1,1,1-trichloroethane data in Table II. Since the triple-point temperature of each solute is well above the critical temperature of oxygen these systems are qualitatively similar to the methane–benzene binary reported previously (*1*). These are systems in which the critical locus and the three-phase S–L–V univariant curves intersect at singular end points with critical identity of the liquid and vapor phases. The experimental data given here are for the solid–liquid or solid–vapor two-phase regions. The measured solubilities are therefore both temperature and pressure dependent; the pressure dependence is considerably weaker below the critical temperature of the solvent. The solubility at a given temperature was found to be a linear function of the pressure and the value at a corresponding saturated pressure (*3*) was obtained by extrapolation. Since the solute concentration is quite low the saturated pressure of pure oxygen is a reasonable approximation to the actual triple point pressure.

The precision of the data ranges from a few tenths of a percent at the higher concentrations to 27.8% in the worst case. The accuracy can be assumed to follow accordingly except for a systematic difference between data obtained at different periods in the study. Methylene chloride data taken with the 10-cm^3 sample loop and a Tenax-GC separation column were 3.8–5.5% greater than similar data obtained with a 5-cm^3 sample loop and a Carbowax 400 on Chromosorb T column. Time and funds did not allow resolution of this descrepancy.

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Glossary

L	liquid phase
S	solid phase
V	vapor phase
x_{exptl}	experimental solute concentration
$x_{\text{sat.}}$	solute concentration in the saturated liquid

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Excess Thermodynamic Functions for Ternary Systems. 3. Total Pressure Data and G^E for Acetone–Acetonitrile–Methyl Acetate at 50 °C

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Isothermal P–x data for the ternary system acetone–acetonitrile–methyl acetate at 50 °C are reported. Data are also presented for the constituent binaries at 50 °C. Reduction of the data via Barker's method allows calculation of G^E.

In parts 1 (*6*) and 2 (*9*) of this series of papers we presented data and correlations of H^E, G^E, and S^E for two highly nonideal ternary systems. Here we report VLE data for a much more nearly ideal system, acetone (1)–acetonitrile (2)–methyl acetate (3) at 50 °C. Because of the relatively simple behavior of this system, much less experimental information is required for the ternary mixtures. Thus the data set comprises VLE measurements for the three constituent binaries and for but three runs on the ternary mixtures formed by addition of each pure constituent to an approximately equimolar mixture of the other two.

Data were taken on the total-pressure apparatus described by Gibbs and Van Ness (*5*), modified for ternary systems by the addition of a third piston injector. Several refinements in experimental technique were also adopted for this work. Minor changes in equipment design have made it possible to zero the differential-pressure null indicator and the Texas Instruments pressure gauge between data points and to incorporate into the raw data corrections for the drift in the zeros of these instruments. Additionally, the time required for degassing of the pure chemicals has been greatly reduced by use of a novel distillation degassing technique (*11*).

The acetone, acetonitrile, and methyl acetate were chromatoquality reagents supplied by Matheson Coleman and Bell. Except for degassing, all reagents were used as received, with indicated purities of at least 99.5 mole %.

Table I. Total Pressure Data for Acetone (1)-Acetonitrile (2) at 50 °C

x_1	x_2	P, mmHg
0.0000	1.0000	253.89
0.0824	0.9176	283.94
0.1600	0.8400	311.02
0.2531	0.7469	346.15
0.3451	0.6549	379.82
0.4314	0.5686	411.59
0.4754	0.5246	425.83
0.5077	0.4923	438.83
0.5517	0.4483	453.07
0.6350	0.3650	482.21
0.7386	0.2614	519.07
0.8138	0.1862	546.56
0.8996	0.1004	578.20
0.9581	0.0419	599.34
1.0000	0.0000	615.16

Results and Correlations

Tables I through III contain experimental total-pressure data for the three constituent binaries; Table IV contains results for the three ternary runs.

Except for the acetone (1)–acetonitrile (2) system, whose P–x behavior closely follows Raoult's law, all data were reduced by Barker's method (*2*). Liquid-phase nonidealities for the binary systems are adequately described by the two-parameter Margules equation

$$g_{ij} \equiv G^{E}{}_{ij}/RT = x_i x_j (A_{ji} x_i + A_{ij} x_j) \tag{1}$$

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