(10) Nelson, D. L., Irish, D. E., *J. Chem. Phys.*, **54**, 4479 (1971).
(11) Osborne, N. S., Stimson, H. F., Ginnings, D. C., *Natl. Bur. Stand.* (*U.S.*), *J. Res.*, **23**, 197 (1939).
(12) Peppard, D. F., Mason, G. W., Hucher, I., *J. Inorg. Nucl. Chem.*, **24**, 881 (1962).
(13) Randall, M., Rossini, F. P., *J. Am. Chem. Soc.*, **51**, 323 (1929).
(14) Rard, J. A., Shiers, L. E., Heiser, D. J., Spedding, F. H., *J. Chem. Eng. Data*, **22**, 337 (1977).
(15) Rard, J. A., Spedding, F. H., *J. Phys. Chem.*, **79**, 257 (1975).
(16) Rueben, J., Fiat, D., *J. Chem. Phys.*, **51**, 4909 (1969).
(17) Rumanova, J. M., Volldina, G. F., Belov, N. V., *Kristallografiya*, **9**, 624 (1964); translated in *Crystallography*, **9**, 545 (1965).
(18) Spedding, F. H., Baker, J. L. Walters, J. P., *J. Chem. Eng. Data*, **20**, 189 (1975).
(19) Spedding, F. H., Czejka, D. A., DeKock, C. W., *J. Phys. Chem.*, **70**, 2423 (1966).
(20) Spedding, F. H., Cullen, P. F., Habenschuss, A., *J. Phys. Chem.*, **78**, 1106 (1974).
(21) Spedding, F. H., Derer, J. L., Mohs, M. M. Rard, J. A., *J. Chem. Eng. Data*, **21**, 474 (1976).
(22) Spedding, F. H., Jaffe, S., *J. Am. Chem. Soc.*, **76**, 884 (1954).
(23) Spedding, F. H., Jones, K. C., *J. Phys. Chem.*, **70**, 2450 (1966).
(24) Spedding, F. H., Mohs, M. M., Derer, J. L., Habenschuss, A., *J. Chem. Eng. Data*, **22**, 142 (1977).
(25) Spedding, F. H., Pickal, M. J., Ayers, B. O., *J. Phys. Chem.*, **70**, 2440 (1966).
(26) Spedding, F. H., Saeger, V. W., Gray, K. A., Boneau, P. K., Brown, M. A., DeKock, C. W., Baker, J. L., Shiers, L. E., Weber, H. O., Habenschuss, A., *J. Chem. Eng. Data*, **20**, 72 (1975).
(27) Spedding, F. H., Shiers, L. E., Brown, M. A., Baker, J. L., Gutierrez, L., McDonald, L. S., Habenschuss, A., *J. Phys. Chem.*, **79**, 1087 (1975).
(28) Spedding, F. H., Shiers, L. E., Brown, M. A., Derer, J. L., Swenson, D. L., Habenschuss, A., *J. Chem. Eng. Data*, **20**, 81 (1975).
(29) Spedding, F. H., Shiers, L. E., Rard, J. A., *J. Chem. Eng. Data*, **20**, 88 (1975).
(30) Spedding, F. H., Walters, J. P., Baker, J. L., *J. Chem. Eng. Data*, **20**, 439 (1975).
(31) Templeton, D. H., Dauben, C. H., *J. Am. Chem. Soc.*, **76**, 5237 (1954).

Received for review January 8, 1979. Accepted May 11, 1979. This work supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

Solubility of Carbon Dioxide in Silicone Oil

Gary D. Wedlake* and Donald B. Robinson

Department of Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

The solubility of CO_2 in a Dow Corning FS-1265, 300 cS silicone oil has been determined at 22 °C as a function of CO_2 pressure. Results indicate solubility increases with pressure and thus high-pressure systems containing CO_2 cannot be considered isolated if they are in contact with this or similar oils.

In our work related to *V–L* equilibria of hydrocarbon systems at high pressures we have investigated a sampling arrangement in which a silicone oil was used to compress the system. We believe that a result from this investigation is of general interest but in particular it has a bearing on the decomposition pressures of sodium bicarbonate as recently observed by Templeton.[1]

The use of silicone oil in our and other applications arises out of its generally low vapor pressure and its chemical stability. However, an additional requirement in our application is that components of the hydrocarbon system not be soluble in the silicone oil at high pressures.

We have measured the solubility of Linde, commercial grade (99.5% pure) CO_2 in a freshly degassed sample of Dow Corning FS-1265, 300 cS silicone oil at room temperature (21.8 ± 0.4 °C). (Dow Corning FS-1265 silicone oil is a trade name for trifluoropropylmethylsiloxane. The structure and the physical properties of this material have been described elsewhere.[2-4] Two density determinations (78.019 ± 0.003 lb/ft^3) of the material used in this work at 22.0 °C are in good agreement with the literature value[4] (78.0 lb/ft^3 at 25.0 °C).) Measurements were made through mass balances within a stainless steel apparatus made up of high-pressure bombs, two Heise gages, interconnecting manifold, and associated valves. Volumes within different sections of the apparatus were determined either by gravimetric procedures using water or by the expansion of Linde research grade (99.993% pure) N_2. (Physical properties of N_2 were taken from tables by Jacobsen and Stewart.[5])

Pressures and temperatures for individual measurements are believed to be accurate to within ±1 psi and ±0.1 °C, respectively. Variation in determining section volumes was less than 0.2%.

Incremental CO_2 solubilities were determined by the mass of CO_2 which desorbed under a reduced pressure or by the mass of CO_2 which was adsorbed under an increased pressure. Mass balances were determined by using CO_2 densities calculated by the correlation reported by Bishnoi et al.[6]

Table I. Solubility of CO_2 in Silicone Oil at 22 °C

total pressure, psia	wt of CO_2 dissolved in 0.1495 lb of silicone oil, lb × 10^2	ratio of CO_2 wt to silicone oil wt, lb of CO_2/lb of silicone oil
109.5	0.35	0.023
160.0	0.57	0.038
230.0	0.92	0.061
289.0	1.27[a]	0.085
325.8	1.46	0.098
446.0	2.35	0.157
587.3	3.86	0.258
691.0	5.71	0.382
775.9	8.67	0.580
833.7	13.38	0.895

[a] Determined by an absorption measurement. All others were determined by desorbing CO_2 from the silicone oil.

Initially, the entire apparatus was rocked for 12 h before measurements were made. This interval was later shortened to 8 h when the additional time was shown to have no significant effect on the final pressure above the silicone oil.

The experimental results are reported in Table I. An analysis of random error in these measurements indicates that the precision of the reported solubility is ±3%. The data, also shown in Figure 1, have a limiting slope at 0.0 psia of 2.1 × 10^{-4} lb of CO_2 lb^{-1} of silicone $psia^{-1}$. This value is in good agreement with a value of 2.20 × 10^{-4} lb of CO_2 lb^{-1} of silicone $psia^{-1}$ reported by Dow Corning in a private communication. Since calculations assume ideal mixing of silicone oil and liquid CO_2, nonidealities may introduce a small systematic error at high CO_2 concentrations.

In the reference cited above, Templeton has reported equilibrium pressures associated with the thermal decomposition of sodium bicarbonate. As shown in his Figure 2, the dissociation pressure is characterized by three discontinuities in addition to being a function of the vapor to solid volume ratio, V_g/V_s, inside the bomb.

0021-9568/79/1724-0305$01.00/0

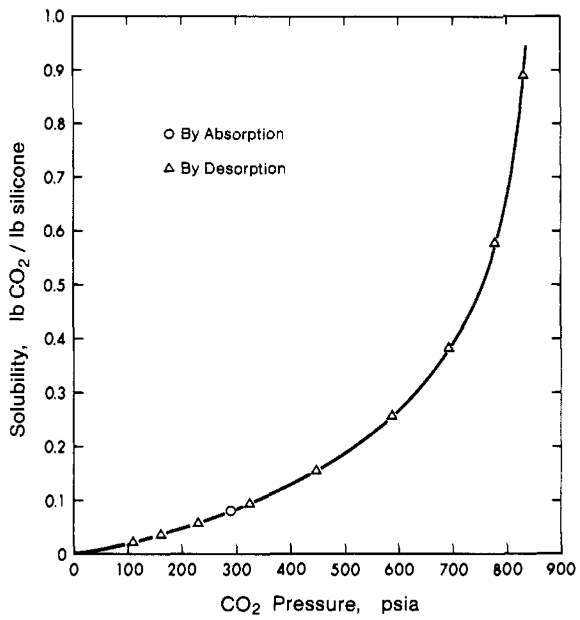

Figure 1.

In the temperature range below the first discontinuity the author states that the decomposition is represented solely by the reaction

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g) \qquad (1)$$

and as such the phase rule dictates that the system contains only one degree of freedom.

However, an inspection of Figure 2 indicates that the dissociation pressure in this region is a function of both temperature and the ratio V_g/V_s. The author does not explain this discrepancy.

As shown in Figure 1 of Templeton's apparatus, a slug of silicone oil is used in the tube connecting the Heise gage to the heated bomb. In view of our results, if this quantity of silicone were large, appreciable quantities of CO_2 could be dissolved in the oil and the assumption of equimolar CO_2 and H_2O concentrations would be invalidated. Under these circumstances the system would contain a second degree of freedom and thus provide an explanation for the observed behavior.

The Peng-Robinson equation[7] predicts a dew point curve for an equimolar mixture of CO_2 and H_2O which may be represented by

$$\ln P = 16.9913 - 5074.96/T \qquad (2)$$

where P is pressure, psia, and T is temperature, K. Since most of Templeton's data are found to be at higher pressures than those predicted by eq 2, it appears that partial condensation also occurs inside the bomb.

While this latter consideration may prove to be the most significant source of discrepancy in this case, the general conclusions of this paper remain valid and careful consideration should be given to CO_2 solubility when relevant.

Literature Cited

(1) Templeton, C. C., *J. Chem. Eng. Data*, **23**, 7 (1978).
(2) Schiefer, H. M., Van Dyke, J., *ASLE Trans.*, **7**, 32 (1964).
(3) Schiefer, H. M., Azzam, H. T., Miller, J. W., *Lubr. Eng.*, **25**, 210 (1969).
(4) Dow Corning Corp. trade publication, "Information about Silicone Fluids", Form No. 22-053-76.
(5) Jacobsen, R. T., Stewart, R. B., *J. Phys. Chem. Ref. Data*, **2**, 757 (1973).
(6) Bishnoi, P. R., Miranda, R. D., Robinson, D. B., *Hydrocarbon Process.*, **53**, 197 (1974).
(7) Peng, D-Y., Robinson, D. B., *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).

Received for review January 8, 1979. Accepted May 3, 1979.

Solid Hydrocarbon Solubility in Liquid Methane–Ethane Mixtures along Three-Phase Solid–Liquid–Vapor Loci

David L. Tiffin, James P. Kohn,* and Kraemer D. Luks

Department of Chemical Engineering, University of Notre Dame, Notre Dame, Indiana 46556

Three ternary systems, methane–ethane–*n*-octane, methane–ethane–benzene, and methane–ethane–cyclohexane, are investigated along their three-phase S–L–V loci. The dramatic solubility enhancement of these solid hydrocarbons in liquid methane due to the presence of ethane is documented and presented graphically for a wide range of ethane concentration levels. Pressure, temperature, liquid-phase molar volume, and liquid-phase composition are tabulated in raw data form.

Introduction

Solid solubility data of hydrocarbon components in low molecular weight solvents are important for use in the design of liquefaction, vaporization, and transport systems for liquefied natural gas (LNG) and liquefied petroleum gas (LPG). The authors are engaged in an extended program of obtaining such data along solid–liquid–vapor loci, primarily in the low solute concentration range.

The solubility of hydrocarbons (*n*-pentane and higher) in liquid methane is quite low in methane-rich binary systems (for example, see ref 6 and 7); on the other hand, the solubility of these same hydrocarbons in liquid ethane (*5*, *10*) is considerably closer to ideal. It follows that, in a ternary S–L–V system with a solvent liquid mixture of methane and ethane, one would expect an increase in the solubility of the hydrocarbon solute over that of a binary system in which pure methane is the solvent liquid. However, it has been observed that, for modest additions of ethane, propane, or *n*-butane to liquid methane, the solubility of hydrocarbons is enhanced significantly beyond what one would reasonably expect by using simple combinatorial rules (*11*, *12*). The solubilities of the hydrocarbon solutes *n*-heptane and *n*-octane were studied in the solvent mixtures of methane–ethane in ref 12 and in solvent mixtures of methane–propane and of methane–*n*-butane in ref 11. In these studies, the data are tabulated, and the solute composition in the liquid phase is

0021-9568/79/1724-0306$01.00/0