J. Chem. Eng. Data **1996,** *41,* 923−925

Solubilities of Diamondoids in Supercritical Solvents

Vicky S. Smith and Amyn S. Teja*

School of Chemical Engineering and Fluid Properties Research Institute, Georgia Institute of Technology,
Atlanta, Georgia 30332-0100

The solubilities of the diamondoids, adamantane and diamantane, in carbon dioxide, ethane, and methane have been measured using a flow apparatus at 333 K (the solubility of diamantane in methane was measured at 353 K) and pressures ranging from 5.31 MPa to 20.10 MPa. The data were correlated as functions of the solvent density and also using the Patel−Teja equation of state. Solubility enhancement for each diamondoid followed regular behavior with respect to the solvent density.

Introduction

The natural gas industry is becoming increasingly concerned with heavy hydrocarbon solids that are obtained during natural gas production from associated gas and petroleum wells. These solids tend to deposit out of the natural gas stream onto pipeline walls, leading to costly problems such as corrosion and plugging of the pipeline.

Diamondoid hydrocarbons are ringed compounds which have a diamond-like structure consisting of a number of six-member carbon rings fused together (Wingert, 1992). They have high melting points and low strain energy, which highlights their relative stability (Fort, 1960). The mechanics of petroleum formation leads to an environment that favors diamondoid precipitation. Therefore, the solubility behavior of the diamondoid solids in natural gas components is of considerable practical interest. For example, operating problems due to the pipeline deposition of diamantane have been noted at a gas field in Canada (King, 1988).

Adamantane and diamantane are the first two "adamantalogs" in the diamondoid series, and the most prevalent diamondoid compounds in natural gas. For this work, their solubilities have been measured in methane, ethane, and carbon dioxide, which are three major components of natural gas.

Experimental Section

A supercritical flow technique similar to that used by Johnston and Eckert (1981), Kurnik *et al.* (1981), Moradinia and Teja (1986), and Schmitt and Reid (1988) was used in this work to obtain solid−fluid phase equilibrium data. In this method, the solvent gas flows over the stationary solid solute at a specified temperature and pressure and the amount of dissolved solute is obtained gravimetrically after depressurization of the loaded solvent stream.

The flow apparatus used to measure solubilities is shown in Figure 1. For experiments in which methane was the solvent, the methane gas was compressed from the cylinder with a gas compressor (Haskel model AG-152) into a surge tank, from which it was delivered to a syringe pump (ISCO model 500D). Carbon dioxide and ethane were liquified and delivered directly from the gas cylinder to the syringe pump.

From the syringe pump, the solvent was delivered at the set-point pressure to the saturator (Jerguson view cell 17-T-40), which contained alternating layers of solute and glass beads to increase solute−solvent contact. The saturator was suspended in a constant-temperature bath, controlled by a liquid heater/circulator (Haake model E3). The temperature inside the saturator was measured with a type T thermocouple calibrated with a NIST-certified standard platinum resistance thermometer (Chino Corp. model R800-3) to the ITS-90 standard. The pressure in the system was measured with an analog bourdon-tube gauge (Heise model CM-51917) calibrated with a dead weight tester (Budenberg model 380H). The estimated uncertainties in the temperature and pressure measurements were ±0.3 K and ±0.05 MPa, respectively.

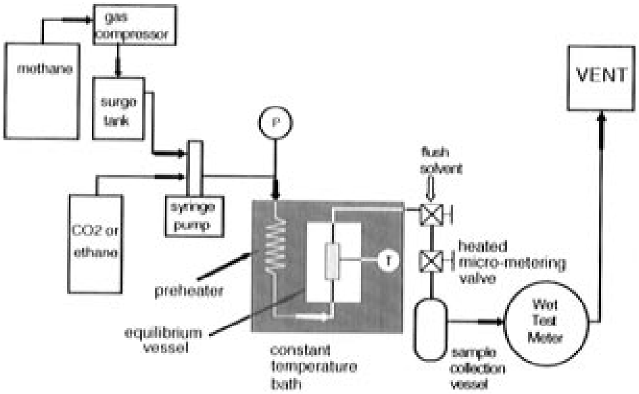

Figure 1. Flow apparatus.

The saturated stream exiting the saturator was then depressurized across a micrometering valve (Whitey model SS-21RS2), and the solute was collected in a sample collection vessel, which was immersed in a low-temperature bath of ethanol and dry ice. The vessel outlet was packed with glass wool to prevent solute from leaving the vessel, and the mass of the solute in the vessel was obtained gravimetrically. The exiting gas stream passed through a wet test meter (Precision Scientific model 63111) for the measurement of the total amount of solvent. The wet test meter was factory-calibrated and certified accurate to ±0.5%.

Materials. Carbon dioxide was obtained from Holox with a stated purity of 99.99+%. Ethane and methane were obtained from Matheson Gas Products at a stated purity of 99.0%. Adamantane was obtained from Aldrich Chemical Co. with a stated minimum purity of 99%. Diamantane was purified by Paul Bryan of Chevron Research and Technology to a stated minimum purity of 99%. Adamantane and diamantane purities were verified by GC−MS, and the chemicals were used without further purification.

S0021-9568(96)00085-4 CCC: $12.00 © 1996 American Chemical Society

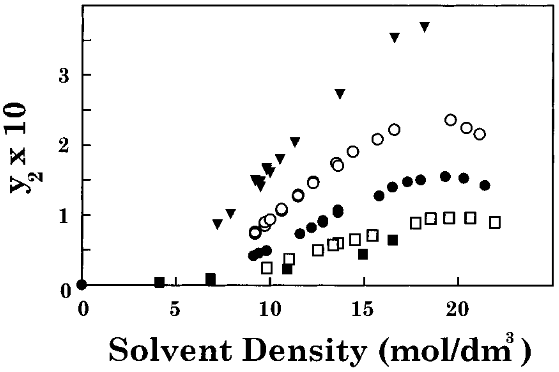

Figure 2. Comparison of solubilities of adamantane in CO_2: (■), this work (333 K); Swaid *et al.* (□) (343 K), (●) (362.5 K), (○) (382 K), (▼) (402 K).

Table 1. Experimental Solubility of Adamantane in CO_2, CH_4, and C_2H_6 at 333 K

CO_2		CH_4		C_2H_6	
/MPa	$y_2 \times 10^4$	P/MPa	$y_2 \times 10^5$	P/MPa	$y_2 \times 10^3$
7.70	4.13 ± 0.35	5.62	8.27 ± 1.23	6.07	3.75 ± 0.23
10.17	8.85 ± 0.38	7.64	7.18 ± 2.66	8.10	8.73 ± 0.06
12.59	23.3 ± 0.78	10.14	6.17 ± 1.28	11.04	18.8 ± 0.70
16.65	43.9 ± 1.39	12.58	15.5 ± 1.54	12.72	26.5 ± 0.35
20.06	64.0 ± 1.02	15.27	25.9 ± 0.88	15.93	34.3 ± 0.31
		16.57	36.8 ± 3.18	20.06	38.4 ± 0.26
		20.08	42.3 ± 5.72		

Table 2. Experimental Solubility of Diamantane in CO_2 and C_2H_6 at 333 K and CH_4 at 353 K

CO_2		CH_4		C_2H_6	
/MPa	$y_2 \times 10^5$	P/MPa	$y_2 \times 10^5$	P/MPa	$y_2 \times 10^4$
8.13	2.95 ± 1.00	17.37	7.08 ± 1.89	7.65	5.25 ± 0.40
10.14	5.69 ± 0.89	18.06	7.26 ± 1.52	10.10	13.8 ± 0.34
12.62	17.5 ± 1.12	19.77	8.43 ± 3.00	13.13	27.3 ± 0.76
15.12	36.9 ± 1.90	20.09	10.9 ± 3.98	16.58	63.4 ± 1.18
17.55	55.3 ± 3.43			20.06	52.4 ± 0.99
20.10	70.8 ± 3.52				

Results and Discussion

The experimental solubilities of adamantane ($C_{10}H_{16}$) in ethane, carbon dioxide, and methane at 333 K are presented in Table 1, whereas solubility data for diamantane H_{20}) in ethane and carbon dioxide at 333 K and in methane at 353 K are presented in Table 2. The solubility of diamantane in methane has been measured at a slightly higher temperature in this work because of the very low solubility at 333 K. Solubility data for these systems are reported in terms of the solute mole fraction y_2 in the supercritical phase. Most of the reported solubility data points represent an average of three measurements. In general, the three replicates agreed to within 5%, except in systems in which the solute mole fraction was of the order of 10^{-5}. For the latter systems, larger errors are to be expected (see Johnston et al., 1982). Each data point in Table 2 is listed with an estimate of experimental uncertainty, obtained from an error analysis that takes account of uncertainties in pressure, temperature, volume, and mass measurements. A detailed explanation of the analysis is given elsewhere (Smith, 1995).

The solubility data for adamantane in carbon dioxide are plotted in Figure 2 with the previously published data of Swaid *et al.* (1985). The solvent densities were obtained from Angus *et al.* (1976). The data measured in this study are represented by the filled squares and are at the lowest temperature included on this graph. These data follow the same trends and are generally consistent with the data of Swaid *et al.* (1985).

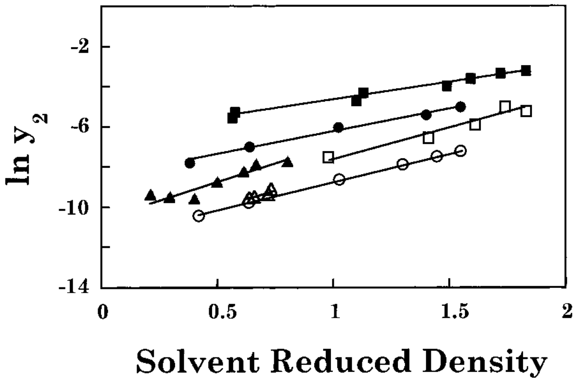

Figure 3. Diamondoid solubilities versus solvent reduced density: (■) adamantane + C_2H_6 (333 K); (●) adamantane + CO_2 (333 K); (□) diamantane + C_2H_6 (333 K); (▲) adamantane + CH_4 (333 K); (△) diamantane + CH_4 (353 K); (○) diamantane + CO_2 (333 K).

Table 3. Correlation of the Solubility of Diamondoids in Supercritical Solvents

system	slope	intercept	R^2
adamantane + CO_2	2.269	−8.558	0.991
adamantane + CH_4	3.510	−10.49	0.873
adamantane + C_2H_6	2.019	−6.891	0.981
diamantane + CO_2	2.791	−11.58	0.999
diamantane + CH_4	3.817	−12.01	0.784
diamantane + C_2H_6	3.017	−10.56	0.953

The solubility data for the six systems measured in this study are plotted in Figure 3 versus the reduced density of the solvent. Solvent critical densities were obtained from Reid *et al.* (1987). Trends are linear, as shown in Figure 3, which also shows that the diamondoid solubilities increase with density at 333 K (or 353 K) in the range of pressures studied. The statistics of the linear fits are given in Table 3. The solubility of the heavier compound diamantane was found to be less than that of adamantane in the same solvent, as expected.

The measured solubilities are much greater than predicted, assuming ideal gas behavior. The extent to which solubility is enhanced is shown by an examination of the enhancement factors E of the solutes, where

$$E = \frac{y_2 P}{P_2^{\mathrm{sat}}} \qquad (1)$$

and y_2 is the experimental solubility of the solute, P is the total system pressure, and P_2^{sat} is the saturation (or, for solid solutes, sublimation) pressure of the pure solute. Sublimation pressures for adamantane and diamantane were obtained from Cullick *et al.* (1994). Enhancement factors versus solvent-reduced density are plotted in Figure 4 for the systems in which carbon dioxide or ethane was the solvent, and linear fits of the data are shown for each solute. Solubility enhancement increases as the solvating power (density) of the solvent increases.

The calculated enhancement factors for the systems studied in this work were found to be greater for the higher molecular weight diamantane, because the sublimation pressure of this substance is lower. Diamantane enhancement in both solvents exhibited the same general trend, as shown by the trend line on the graph through both sets of diamantane measurements. Adamantane enhancement in both carbon dioxide and ethane also exhibited a linear trend. The slopes of the trend lines for each solute in methane were different from the slopes of the trend lines for each solute in carbon dioxide and ethane, because of

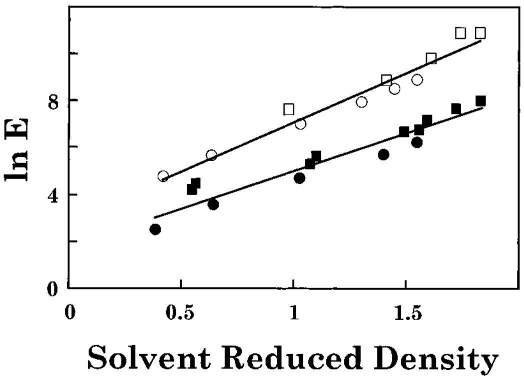

Figure 4. Solute enhancement factor versus solvent-reduced density: (■) adamantane + C_2H_6; (●) adamantane + CO_2; (□) diamantane + C_2H_6; (○) diamantane + CO_2.

Table 4. Correlation of the Solubility of Diamondoids in Supercritical Solvents Using the Patel–Teja Equation of State

	vdW1		vdW2		
system	k_{ij}	% AAD	k_{ij}	l_{ij}	% AAD
$_6 + C_{10}H_{16}$	0.025 30	17.49	0.057 47	0.063 67	16.45
$+ C_{10}H_{16}$	0.150 33	23.47	0.270 90	0.293 86	3.40
$+ C_{10}H_{16}$	0.226 95	55.34	1.1913	2.971 7	26.84
$_6 + C_{16}H_{20}$	0.005 56	20.08	0.049 55	0.109 56	19.81
$+ C_{16}H_{20}$	0.130 82	18.43	0.219 92	0.244 30	11.90
$+ C_{16}H_{20}$	0.048 67	6.83	0.153 09	0.286 42	6.93

the difference in reduced temperature between methane and the other solvents.

Solubilities for the six systems were correlated using the equation of state of Patel and Teja (1982) (PT EOS). The critical temperatures and pressures of the solutes, which are required by the PT EOS, have not been measured because the substances decompose below their critical points. Instead, these values have been estimated by averaging the results of two group contribution methods—those of Ambrose (1978 and 1979) and Joback (as reported in Reid *et al.*, 1987). In both methods, critical temperature is a function of normal boiling point. Normal boiling points for each diamondoid were obtained from Wingert (1992).

The mixture constants for the PT EOS were calculated using several mixing rules. Results of the calculations using classical one- and two-parameter van der Waals mixing rules are summarized in Table 4. The one-parameter mixing rule (denoted by vdW1 in Table 4) contains one adjustable parameter k_{ij} in the cross-term a_{ij} as follows:

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{2}$$

whereas the two-parameter rule (denoted by vdW2 in Table 4) introduces a second adjustable parameter l_{ij} in the calculation of b_{ij} as follows:

$$b_{ij} = \frac{1}{2}(b_i + b_j)(1 - l_{ij}) \tag{3}$$

The objective function (OF) used to obtain the adjustable parameters from experimental data for each mixing rule is

$$\text{OF} = \sum_i \frac{(y_{i,\text{calc}} - y_{i,\text{exp}})^2}{{\sigma_{\Delta y_i}}^2} \tag{4}$$

where σ is the experimental uncertainty of each data point.

Each mixing rule was evaluated by examining the percent average absolute deviation (% AAD) between experimental and correlated solubilities, as follows:

$$\%\ \text{AAD} = \frac{100}{N}\sum_i \frac{|y_{i,\text{calc}} - y_{i,\text{exp}}|}{y_{i,\text{exp}}} \tag{5}$$

where N is the total number of data points per system. The results for each mixing rule, including the optimized parameters and % AAD for each system, are given in Table 4. One binary interaction parameter was sufficient to correlate the solubilities in five of the systems studied. However, the CH_4–adamantane system could not be correlated satisfactorily even with two adjustable parameters.

Acknowledgment

The authors wish to thank Dr. Robert Enick at the University of Pittsburgh for his help in obtaining reference materials for this publication.

Literature Cited

Ambrose, D. Correlation and Estimation of Vapour-Liquid Critical Properties. I. Critical Temperatures of Organic Compounds. NPL Report Chemistry 92; National Physical Laboratory: Teddington, U.K., 1978.

Ambrose, D. Correlation and Estimation of Vapour-Liquid Critical Properties. II. Critical Pressures and Volumes of Organic Compounds; NPL Report Chemistry 98; National Physical Laboratory: Teddington, U.K., 1979.

Angus, S.; Armstrong, B.; de Reuck, K. M. *Carbon Dioxide: International Thermodynamic Tables of the Fluid State*; Pergamon Press: Oxford, U.K., 1976.

Cullick, A. S.; Magouirk, J. L.; Ng, H. J. An Analysis of Solid-Forming Characteristics from a Produced Gas Stream. Presented at the 73rd Annual Convention of the Gas Processors Association, New Orleans, 1994.

Fort, R. C., Jr. *Adamantane The Chemistry of Diamond Molecules*; Marcel Dekker, Inc.: New York, 1960.

Johnston, K. P.; Eckert, C. A. An Analytical Carnahan-Starling-van der Waals Model for Solubility of Hydrocarbon Solids in Supercritical Fluids. *AIChE J.* **1981**, *27*, 773–779.

Johnston, K. P.; Ziger, D. H.; Eckert, C. A. Solubilities of hydrocarbon solids in supercritical fluids. The Augmented van der Waals Treatment. *Ind. Eng. Chem. Fundam.* **1982**, *21*, 191–197.

King, W. J. Operating Problems in the Hanlan Swan Hills Gas Field (SPE paper 17761). *Proceedings—Gas Technology Symposium, Dallas, TX*; SPE: Brookfield, CT, 1988, 469–474.

Kurnik, R. T.; Holla, S. J.; Reid, R. C. Solubility of Solids in Supercritical Carbon Dioxide and Ethylene. *J. Chem. Eng. Data* **1981**, *26*, 47–51.

Moradinia, I.; Teja, A. S. Solubilities of Solid n-Octacosane, n-Triacontane and n-Dotriacontane in Supercritical Ethane. *Fluid Phase Equilib.* **1986,** *28*, 199–209.

Patel, N.; Teja, A. S. A New Cubic Equation of State for Fluids and Fluid Mixtures. *Chem. Eng. Sci.* **1982**, *37*, 463–473.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1987.

Schmitt, W. J.; Reid, R. C. The Solubility of Paraffinic Hydrocarbons and Their Derivatives in Supercritical Carbon Dioxide. *Chem. Eng. Commun.* **1988,** *64*, 155–176.

Smith, V. S. Ph.D. Thesis, Georgia Institute of Technology, 1995.

Swaid, I.; Nickel, D.; Schneider, G. M. NIR Spectroscopic Investigations on Phase Behaviour of Low-Volatile Organic Substances in Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1985**, *21*, 95–112.

Wingert, W. S. G.C.-M.S. Analysis of Diamondoid Hydrocarbons in Smackover Petroleums. *Fuel* **1992**, *71*, 37–43.

Received for review March 4, 1996. Accepted May 3, 1996.[⊗] The authors gratefully acknowledge the financial support of the Gas Research Institute and the Gas Processors Association for this work.

JE960085C

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.