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Experimental Data Assessment Test for Diamondoids Solubility in Gaseous System

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ABSTRACT: Deposition of solid diamond-like hydrocarbons may cause drastic problems in natural gas systems, and therefore it is of interest to know deposit conditions as accurately as possible. Unfortunately, only a few sets of experimental data for solubility of diamondoids in gaseous systems have been reported in the literature partly because of the difficulties in measurements of very low concentrations of the latter compounds in the gas phase. Thus, the reliability of the corresponding data must be checked prior to their applications. In this communication, we present the results of a thermodynamic assessment test (consistency test) based on an area test approach for experimental solubility data of adamantane and diamantane in supercritical carbon dioxide and ethane. The modified Esmaeilzadeh−Roshanfekr (m-ER) cubic equation of state (CEoS) along with the vdW2 mixing rules are used to model the solubility of the aforementioned diamondoids in the latter supercritical gases. The results show that all of the investigated experimental data sets seem to be thermodynamically consistent.

INTRODUCTION

A serious problem in the natural gas industry is deposition of solids in the formation, in well bores, and in production facilities especially at high temperature and pressure conditions, especially during development of new natural gas/gas condensate reservoirs.[1,2] As a consequence, solid deposition leads to increasing production/operating/maintenance costs and finally a low gas production rate. Moreover, considering safety margins in the design of the related equipment accounting for these depositions imposes another excess costs and time on the projects.[1,3]

Diamondoid cage hydrocarbons are ringed compounds containing a diamond-like structure consisting of a number of six-membered carbon rings fused together.[1,3−5] They have highly symmetrical, strain-free structures and high melting points, which demonstrate their relative stability.[1,4−6] As mentioned earlier, the pressure−temperature conditions in natural gas production/processes may result in deposition of these compounds. Therefore, the solubility behavior of the diamondoid solids in natural gases is of great interest.[1,3] Furthermore, applications of diamondoids as nontoxic and controllable nanostructures have also been reported in the literature especially in the field of molecular manufacturing in nanotechnology.[5]

Regarding the aforementioned significances, thermodynamic models based on accurate experimental data of solubility of diamondoids in gaseous systems are needed to reliably determine the phase behavior of these compounds during natural gas production/processing. In other words, measuring accurate experimental data on corresponding phase behaviors is of great interest. However, several error sources in experimental measurements including calibration of pressure transducers, temperature probes, and detectors of gas chromatographs and possible errors during the measurements of phase equilibria especially those dealing with low concentrations, improper design of the equipment, etc. may lead to unreliable experimental data.

This work aims at testing the thermodynamic consistency of literature data for the solubility of two common diamondoids (adamantane and diamantine) in supercritical carbon dioxide and ethane. An area test approach derived from the “Gibbs−Duhem equation”[7−20] is used for this purpose. It is expected that this study provides a better understanding of diamondoids solubility in the natural gas system.

THERMODYNAMIC CONSISTENCY TEST

The thermodynamic relationship, which is frequently used to analyze thermodynamic consistency of experimental phase equilibrium data, is the fundamental “Gibbs−Duhem equation”.[7−20] This equation, as presented in the literature, interrelates the activity/fugacity coefficients of all components in a given mixture. If this equation is not obeyed within the defined criteria then the data are declared to be thermodynamically inconsistent. It means that this relation imposes a constraint on the activity/fugacity coefficients that are not satisfied by the experimental data.[7−20] This is partly due to various errors occurring during experimental works especially those dealing with high pressures, time-consuming phase transitions, compositional gradients, hysteresis, etc.[21−23]

The ways in which the “Gibbs−Duhem equation”[7−20] is arranged and applied to the experimental data have given origin to several “Consistency Test Methods”, most of them designed for low-pressure data. Among these are the “Slope Test”, the “Integral Test”, the “Differential Test”, and the “Tangent-Intercept Test”.[7−20] Good reviews of these methods are given elsewhere.[7−20]

In recent years, Valderrama and co-workers[13−17] have performed thermodynamic consistency tests on various phase equilibrium

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systems. Recently, Eslamimanesh and co-workers[2,7,18,19] have applied almost the same approach for performing the thermodynamic consistency test on significant systems encountered in the petroleum industry, e.g., water content of methane in equilibrium with gas hydrate, liquid water or ice,[18] sulfur content of hydrogen sulfide,[19] wax solubility in gaseous systems,[2] and solubility in carbon dioxide/methane and water system inside and outside the gas hydrate formation region.[7]

The method, which is based on rewriting the "Gibbs−Duhem equation"[7−20] in terms of fugacity coefficients,[2,7,13−20] employed here is considered as a modeling procedure. Accurate representation of the experimental data (i.e., the average deviations of the model results from experimental values are within the acceptable range according to the studied system and the desired purpose) is requested to correctly apply the consistency test. Fitting of the experimental data allows adjustment of some model parameters through minimizing a defined objective function.[2,7,13−20] The basic requirements of a proper data assessment test have been well studied earlier.[2,7,13−20]

Expressions. The "Gibbs−Duhem equation"[7−20] for a binary mixture at constant temperature can be rewritten in terms of the fugacity coefficients as follows[2,7,13−20]

$$\left[\frac{Z-1}{P}\right] dP = y_1 d(\ln \varphi_1) + y_2 d(\ln \varphi_2) \tag{1}$$

where y represents the solute mole fraction in a fluid phase; P stands for pressure; d is the derivative symbol; Z is the compressibility factor; and φ stands for the fugacity coefficient in the related phase. In this equation, subscripts 1 and 2 refer to components 1 and 2, respectively. Equation 1 is rearranged as

$$\frac{1}{P}\frac{dP}{dy_2} = \frac{y_2}{(Z-1)}\frac{d(\ln \varphi_2)}{dy_2} + \frac{(1-y_2)}{(Z-1)}\frac{d(\ln \varphi_1)}{dy_2} \tag{2}$$

or in integral form as follows

$$\int \frac{1}{Py_2}\mathrm{d}p = \int \frac{1}{(Z-1)\varphi_2}\mathrm{d}\varphi_2 + \int \frac{(1-y_2)}{y_2(Z-1)\varphi_1}\mathrm{d}\varphi_1 \tag{3}$$

The properties φ_1, φ_2, and Z can be calculated using an appropriate thermodynamic model.

In eq 3, the left-hand side is designated by A_p and the right-hand side by A_φ, as follows[2,7,13−20]

$$A_\mathrm{p} = \int \frac{1}{Py_2}\mathrm{d}P \tag{4}$$

$$A_\varphi = A_{\varphi 1} + A_{\varphi 2} \tag{5}$$

$$A_{\varphi 1} = \int \frac{(1-y_2)}{y_2(Z-1)\varphi_1}\mathrm{d}\varphi_1 \tag{6}$$

$$A_{\varphi 2} = \int \frac{1}{(Z-1)\varphi_2}\mathrm{d}\varphi_2 \tag{7}$$

Table 1. Physical Properties of the Investigated Compounds[1,3]

	T	$P^{\mathrm{sat}a}$	$v^{\mathrm{s}b} \cdot 10^3$	$T_\mathrm{c}{}^c$	$P_\mathrm{c}{}^d$	
substance	K	MPa	$(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	K	MPa	ω^e
carbon dioxide		-[*]	-	304.13	7.377	0.2239
methane		-	-	190.564	4.599	0.0114
ethane		-	-	305.32	4.872	0.0995
adamantane	333	$2.52 \cdot 10^{-4}$	0.1273	703	2.92	0.185
diamantane	333	$2.21 \cdot 10^{-6}$	0.1554	791	2.26	0.163
	353	$1.37 \cdot 10^{-5}$	0.1554			

[a] Sublimation pressure. [b] Solid molar volume. [c] Critical temperature. [d] Critical pressure. [e] Acentric factor. [*] Not required.

Thus, if a set of data is considered to be consistent, A_p should be equal to A_φ within acceptable defined deviations. To set the margins of error, a percent area deviation $(100 \cdot \Delta A_i/A_i)$ between experimental and calculated values is defined as[2,7,13−20]

$$100 \cdot \Delta A_i/A_i = 100\left[\frac{A_{\varphi_i} - A_{\mathrm{p}_i}}{A_{\mathrm{p}_i}}\right] \tag{8}$$

where i refers to the data set number. The maximum values accepted for these deviations regarding the proposed systems are evaluated using suitable mathematical procedures. The detailed derivations of the preceding equations can be found elsewhere.[2,7,13−20]

THERMODYNAMIC MODEL

Smith and Teja[3] have already shown that the solubility of diamondoids in gaseous systems can be well represented using conventional thermodynamic models adopted for representation of solid compounds in supercritical fluids by applying a three-parameter equation of state (EoS) for evaluation of fugacity coefficients. For phase equilibrium calculations, the equality of the fugacity of solute to its fugacity in supercritical fluid is assumed as follows[1,23]

$$f_i^\mathrm{s} = f_i^\mathrm{supercritical} \tag{9}$$

where f refers to the fugacity; superscript s denotes the solid state; and subscript i stands for ith component in the mixture. Taking into account the following assumptions:[23]

1. the supercritical fluid is assumed to be insoluble in the solid (solute-containing) phase;
2. the molar volume of the solute is pressure-independent;
3. the fugacity coefficient of the solute at saturation is unity, eq 9 is written as[23]

$$P_i^\mathrm{sat} \exp\left[\frac{v_i^\mathrm{s}(P - P_i^\mathrm{sat})}{RT}\right] = y_i \varphi_i P \tag{10}$$

where v is the solid molar volume; R represents the universal gas constant; T refers to temperature; and superscript sat stands for saturation conditions. The values of sublimation pressures (P_i^sat) and solid molar volumes (v^s) are taken from GPA Research Report 171,[1] which have been reported in Table 1 along with other required physical parameters. For evaluation of the fugacity of diamondoids in the gas phase, the modified Esmaeilzade−Roshanfekr (m-ER) cubic three-parameter equation of state (CEoS)[24,25] along with vdW2 mixing rules[8,12,23] has been used. Previous studies[23−26] demonstrated that the calculated/predicted phase behavior in the solid compound + supercritical fluid system using the aforementioned CEoS[24,25] is more accurate than the similar Patel−Teja (PT) EoS.[27] The detailed description of the applied CEoS[24,25] and mixing rules[8,12,23] has been presented in previous articles.[23−26]

Methodology. The following algorithm is applied for the thermodynamic consistency test:[2,7,13−20]

1. Determine A_p from eq 4 using the experimental $P-T-y$ (pressure−temperature−molar composition of diamondoids in the gas phase) data. Use a numerical integration for this purpose. In this work, Simpson's 3/8 rule[28] has been used
2. Evaluate A_φ by eqs 5 to 7 using the obtained values for φ_2 and Z from the thermodynamic model[23] for the proposed system and y_2 from experimental data.
3. For every set of the experimental data, determine an absolute percent area deviation $(100\cdot\Delta A_i/A_i)$ between experimental (A_p) and calculated values $(A_{\varphi i})$ using eq 8.

Consistency Criteria. The deviations of the thermodynamic model results should lie within a defined acceptable range. In this work, the accepted absolute relative deviations (ARDs) for the calculated mole fractions of diamondoids in the supercritical phase (defined by the following equation) are considered to be between (0 and 20) % according to capabilities of the thermodynamic model[23] for this purpose[2,7,13−20]

$$100\cdot\text{ARD} = 100\,\frac{|y_i^{\text{calcd}} - y_i^{\text{exptl}}|}{y_i^{\text{exptl}}} \tag{11}$$

Table 2. Experimental Data[1,3] Ranges Used for Performing the Thermodynamic Assessment Test

				range of data		
system	set no.	T/K	N^a	P/MPa	$y_2{}^c\cdot 10^4$	ref[b]
adamantane + CO_2	1	333	5	7.7 to 20.06	4.13 to 64	1,3
adamantane + CH_4	2	333	3	5.62 to 20.08	0.83 to 4.23	1,3
adamantane + C_2H_6	3	333	5	8.1 to 20.06	37.5 to 384	1,3
diamantane + CO_2	4	333	4	12.62 to 20.1	0.29 to 7.08	1,3
diamantane + CH_4	5	353	4	17.37 to 20.09	0.71 to 1.09	1,3
diamantane + C_2H_6	6	333	3	10.1 to 20.06	5.25 to 52.4	1,3

[a] Number of experimental data. [b] Reference of experimental data. [c] Diomondoids solubility (mole fraction).

where superscripts calcd and exptl refer to calculated and experimental values, respectively.

It is shown that the ARDs percent of the model[23] results from experimental values[1] are generally less than 20 %. Therefore, the model can be considered acceptable for the data assessment test.

Table 3. Calculated Solubility of Diamondoids in the Gaseous System Using the Thermodynamic Model[23]

set no.	T/K	P/MPa	$y_2{}^{\text{exptl}a}\cdot 10^4$	$y_2{}^{\text{calcd}b}\cdot 10^4$	$k_{ij}{}^c$	$l_{ij}{}^c$	ARD[d] %
1	333	7.70	4.13	3.49	0.277	0.283	15.5
		10.17	8.85	8.85			0.0
		12.59	23.30	19.50			16.3
		16.65	43.90	44.55			1.5
		20.06	64.00	64.00			0.0
3	333	6.07	37.50	16.27	0.041	0.036	56.6
		8.10	87.30	87.30			0.0
		11.04	188.00	212.97			13.3
		12.72	265.00	274.13			3.4
		15.93	343.00	342.42			0.2
		20.06	384.00	384.00			0.0
4	333	8.13	0.30	0.15	0.196	0.270	49.6
		10.14	0.57	0.45			20.4
		12.62	1.75	1.75			0.0
		15.12	3.69	3.75			1.7
		17.55	5.53	5.53			0.0
		20.10	7.08	7.07			0.1
6	333	7.65	5.25	3.06	0.034	0.160	41.6
		10.1	13.80	13.80			0.0
		13.13	27.30	27.96			2.4
		16.58	63.40	44.06			30.5
		20.06	52.40	52.40			0.0

[a] Experimental diamondoids solubility in the gas phase (mole fraction). [b] Calculated diamondoids solubility in the gas phase (mole fraction). [c] The order of magnitude of the binary interaction parameters is in agreement with those reported by Smith and Teja.[3] [d] $100\cdot\text{ARD} = 100((|y_2^{\text{calcd}} - y_2^{\text{exptl}}|)/y_2^{\text{exptl}})$.

Table 4. Detailed Results of Thermodynamic Data Assessment Test on the Investigated Experimental Data[1,3]

system	T/K	P/MPa	Z^a	$\varphi_2{}^{gf}$	$\varphi_1{}^{gg}$	$A_p{}^b$	$A_\varphi{}^c$	$100\cdot\Delta A_i/A_i{}^d$	TR[e]
adamantane + CO_2	333	7.70	0.65570	0.11291	0.72589	733.006	586.494	19.988	TC[h]
		10.17	0.52363	0.04154	0.64849				
		12.59	0.43315	0.01558	0.58026				
		16.65	0.42522	0.00694	0.49461				
		20.06	0.45647	0.00494	0.44610				
adamantane + C_2H_6	333	8.10	0.37881	0.00517	0.57718	38.245	35.189	7.990	TC
		11.04	0.38532	0.00178	0.48067				
		12.72	0.41220	0.00129	0.44371				
		15.93	0.47775	0.00096	0.39357				
		20.06	0.56697	0.00082	0.35298				
diamantane + CO_2	333	12.62	0.44345	0.00202	0.58420	1273.873	1182.235	7.194	TC[h]
		15.12	0.42368	0.00091	0.52706				
		17.55	0.43516	0.00061	0.48405				
		20.10	0.45822	0.00047	0.44904				
diamantane + C_2H_6	333	10.10	0.39645	0.00027	0.50506	213.422	166.947	21.777	TC[h]
		13.13	0.49683	0.00008	0.38325				
		20.06	0.56532	0.00007	0.35059				

[a] Compressibility factor. [b] Area of integral related to the experimental data. [c] Area of integral related to the calculated values. [d] Area deviation. [e] Test result. [f] Fugacity coefficient of diamondoids in the gas phase. [g] Fugacity coefficient of supercritical gas. [h] TC: thermodynamically consistent data.

For determination of the acceptable percentages of the two evaluated areas' deviations from each other, the error propagation has been performed on the existing experimental data. This was done using the general equation of error propagation,[28,29] considering the temperature and mole fraction of diamondoids in the supercritical phase as the independent measured variables.[2,7,13−20] The calculated individual area (A_φ) is the dependent variable of interest. The error in the calculated areas, E_A, is calculated as follows[2,7,13−20]

$$E_{\mathrm{A}} = \left[\frac{\partial A_{\varphi j}}{\partial T}\right]\Delta T + \left[\frac{\partial A_{\varphi j}}{\partial y}\right]\Delta y \qquad (12)$$

and consequently the percent error in the areas

$$100\cdot E_{\mathrm{A}} = 100\left[\left|\frac{E_{\mathrm{A}}}{A_{\varphi j}}\right|\right] \qquad (13)$$

where subscript j refers to the jth calculated area and ∂ and Δ are the partial derivative and difference operators, respectively. We assume maximum uncertainties of ± 0.3 K for the experimental temperature and ± 5 % for the experimental solubility data.[1] However, these uncertainties depend on the method of experimental measurements: e.g., the method used by Teja and coworkers[1,3] is based on a dynamic method. The maximum acceptable errors are highly dependent on the uncertainty of solubility measurements, and one can also neglect the first right-hand side term of eq 12. However, the uncertainty for the measurement of solubility of diamondoids is high, and that is why it is justified to perform our thermodynamic consistency test on such data.

Because analytical derivatives are not so simple regarding the expression of the m-ER-EoS[24,25] with vdW mixing rules,[8,12,23] the partial derivatives of the two preceding equations have been evaluated using the central finite difference[28] method. It results in the $100\cdot\Delta A_i/A_i$ between (0 and 23) %. Therefore, the range [0,23] % is established as the acceptable error range of calculated areas (A_i) of thermodynamically consistent data resulting from eqs 4 to 7.

The thermodynamic consistency test criteria are applied based on the steps well-presented in our previous works.[2,7,13−20]

RESULTS AND DISCUSSION

Six experimental isothermal data[1,3] of solubilities of adamantane and diamantane in supercritical carbon dioxide, methane, and ethane have been treated here for the data assessment test. Table 2 summarizes the ranges of the data.

The results of calculations of solubilities of investigated diamondoids in supercritical CO_2 and ethane are shown in Table 3. The tuned binary interaction parameters using the proposed thermodynamic model[23] are also reported in this table. It is implied that the applied model is able to represent four of the experimental solubility data sets within the acceptable absolute deviation range of [0,20] % requested for a successful data assessment test. However, it has been found out that the applied model can not well represent the experimental solubility data of diamondoids for the systems containing methane. This conclusion is in agreement with the previous statement of Smith and Teja[3] regarding these systems with unusual phase behaviors: "However, the CH_4−adamantane system could not be correlated satisfactorily even with two adjustable parameters".[3]

Table 4 reports the results of the thermodynamic consistency test for solubilities of investigated diamondoids in supercritical carbon dioxide and ethane. It should be noted that the data points for which the proposed thermodynamic model does not lead to the deviations within the acceptable range are ignored for the assessment test.

The results show that all of the studied experimental data that are well-represented by the applied thermodynamic model[23] seem to be thermodynamically consistent. This fact demonstrates the capability of the experimental procedure of measuring these solubilities using the dynamic method in spite of several difficulties in such measurements. Another element inferred from the test results is that these measurements have been done with careful calibration of the measuring devices like pressure transducers and temperature probes.

Furthermore, the results of such a test introduce a procedure to select the experimental data by which a thermodynamic model is supposed to be tuned and optimal values of the model parameters are supposed to be obtained. Thermodynamically inconsistent data (sometimes not fully consistent data) used for tuning of the models will bring about inaccurate predictions of the model in further applications, and the cause of such deviations may not be easily figured out.[2,7,13−20]

Moreover, it should be noted that the performed consistency test method has been developed based on the "Gibbs−Duhem equation",[7−20] which holds for homogeneous phases. Due to the fact that the solubility of diamondoids in the gas phase is very low, it is assumed that the gas phase is a homogeneous one. Finally, more meticulous studies should be done to develop thermodynamic models suitable for representation of the solubility data for the methane + diamondoids system. Having applied a proper model, the consistency test of the corresponding data would be possible.

CONCLUSIONS

A thermodynamic data assessment test was applied to the four isothermal experimental data sets[1,3] for solubilities of adamantane and diamantane in supercritical carbon dioxide and ethane. The data assessment test was based on the area test approach derived from the original "Gibbs−Duhem equation"[7−20] at constant temperature. The m-ER CEoS[24,25] with vdw2 mixing rules[8,12,23] was used to model the corresponding solubilities. The results showed that the aforementioned experimental solubility data, which are generally well-represented by the applied model,[23] seem to be thermodynamically consistent. In addition, the results indicated that the measurements of such data must be done accurately and deliberately to be able to use them in tuning of the future thermodynamic models for predictions/representation of solubility of diamondoids in the gaseseous system.

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