Solubilities of Adamantane and Diamantane in Pressurized Hot Water

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Aqueous solubilities of lower diamondoid hydrocarbons, adamantane ($C_{10}H_{16}$) and diamantane ($C_{14}H_{20}$), were measured along the 5 MPa isobar at temperatures between 313 K and the solid–liquid–vapor triple-point temperature of the solute. The activity coefficients of the individual diamondoids in saturated aqueous solutions were estimated from the solubility data employing two different approximations of the pure-solute heat capacity difference ΔC_{P2}. The aqueous solubilities and activity coefficients of diamondoids were compared with those of polycyclic aromatic hydrocarbons with the same carbon numbers. Depending on temperature and on the approximation of ΔC_{P2}, the activity coefficient of adamantane in saturated aqueous solution exceeds that of naphthalene by a factor ranging within 70 to 150, whereas the activity coefficient of diamantane in saturated aqueous solution exceeds that of anthracene by a factor ranging within 10 to 50.

Introduction

Liquid water in the temperature range from the normal boiling point to the critical point, or pressurized hot water (PHW), has recently gained an important place among tunable solvents[1,2] because the solvating abilities of water can be varied widely by adjusting the operating temperature and pressure.[3–6] Detailed characterization of solvent properties of PHW requires diverse experimental data including solubilities of various types of solutes in PHW. In some applications of PHW, such as in environmental remediation or in sample treatment procedures for analytical chemistry, aqueous solubilities of heavy organic nonelectrolyte solids can be important. To date, this kind of experimental data have mostly been available for polycyclic aromatic hydrocarbons (PAHs)[7–14] because of environmental pollution concerns and carcinogenic effects of PAHs. Solubility behaviors of other classes of heavy organic solids in PHW have received much less attention.

From a systematic point of view, PAHs can be pictured as hydrogen-terminated fragments of graphite, the most abundant allotrope of pure carbon. The hydrogen-terminated fragments of another well-known allotrope of carbon, diamond, are called diamondoids. Since the first isolation of the simplest diamondoid, adamantane, from petroleum crude oil deposits near Hodonín (Czech Republic) and Gbely (Slovakia),[15] diamondoids have become an important class of hydrocarbons with promising applications, e.g., as molecular building blocks in nanotechnology.[16,17]

Adamantane was discovered when solving a purely practical problem with high-melting solid deposits during fractional distillation of oil. Later on, similar kinds of problems led to extensive investigations of high-pressure phase equilibria in binary (diamondoid + gas) mixtures[18–20] as well as to determinations of solubilities of diamondoids in supercritical fluids[21,22] and in liquid hydrocarbons.[23]

The purpose of this work is to complement the solubility data for lower diamondoids with aqueous solubilities. The solubilities of solid adamantane ($C_{10}H_{16}$) and solid diamantane ($C_{14}H_{20}$) were measured at pressures close to 5 MPa and temperatures between 313 K and the solid–liquid–vapor triple point of the solute. Aqueous solubilities of diamondoids are compared with those of PAHs with the same carbon numbers. The differences between the diamondoid−water and the PAH−water interactions are discussed in terms of the solute activity coefficients estimated from the solubility data.

Experimental Section

Materials. Adamantane (> 99 %) was purchased from Sigma-Aldrich (Prague, Czech Republic), and diamantane (> 99 %) was obtained from Lachema (Brno, Czech Republic). Both solutes were used as received because the GC/MS analysis of their standard solutions did not indicate the presence of any major impurities. Naphthalene (> 99 %) used as the internal standard for GC/MS was supplied by Sigma-Aldrich (Prague, Czech Republic). Hexane (> 95 %) was obtained from Riedel deHaën (Prague, Czech Republic). Water was purified with a reverse osmosis system Ultra Clear UV (SG Wasseraufbereitung und Regenerierstation, Barsbüttel, Germany).

Apparatus and Procedure. The aqueous solubilities of the individual diamondoids were measured using the apparatus and procedure employed before.[12–14,24] Briefly, a dynamic method was employed to generate the aqueous solution of the solute at the particular temperature and pressure, and a known mass of the solution was allowed to cool to room temperature. The solute was then extracted with hexane, and the organic solution was analyzed by GC/MS employing naphthalene as the internal standard. Any errors caused by the residual amount of the solute in the aqueous phase were safely within the experimental uncertainty as indicated by repeated aqueous–organic equilibration experiments.

The operating procedure was the same as in the previous studies with PAHs[12–14] and aromatic heterocycles.[24] The flow-through extraction cell (length 110 mm, i.d. 4 mm, internal volume 1.4 cm^3) was packed with a mixture of crystalline solute (approximately 0.3 g) with glass beads. In the present study, the dimensions of fused-silica tubing used as the flow restrictor were 1.25 m length and 75 μm i.d. The mass of the individual samples of the aqueous solution ranged within (3 to 7) g, and the mass flow rate of water through the system was always less than 0.017 $g \cdot s^{-1}$. An initial test of the flow-rate dependence of

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Table 1. Aqueous Solubilities of the Solutes x_2 and Their Standard Deviations SD as Functions of Temperature T and Pressure P

solute	T/K	P/MPa	10^9x_2	$10^9\mathrm{SD}^a$
adamantane	313.2	5.2	28.5	2.08
	333.2	5.1	57.2	3.78
	353.2	5.0	143	7.04
	373.2	5.0	407	10.3
	393.2	5.0	1090	40.5
	413.2	5.1	3180	65.0
	433.2	5.0	10500	359
	453.2	5.0	25000	838
	473.2	5.0	65700	2140
	493.2	5.0	170000	6500
diamantane	313.2	5.3	0.912	0.0912
	333.2	5.0	2.51	0.200
	353.2	5.0	11.2	0.530
	373.2	5.0	49.2	1.52
	393.2	5.0	173	10.1
	413.2	5.0	541	17.9
	433.2	5.4	1860	107
	453.2	5.2	5590	192
	473.2	5.0	14600	1070
	493.2	4.8	37700	803

[a] Standard deviations (SD) are based on five fractions collected at each condition.

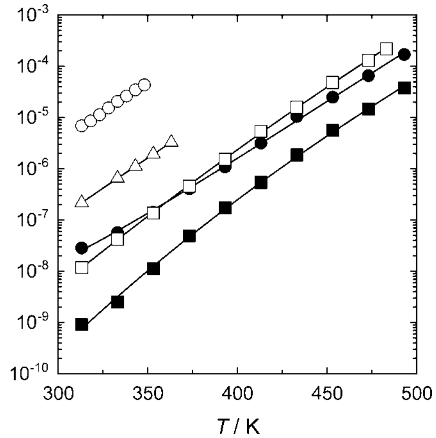

Figure 1. Aqueous solubilities of diamondoids and selected PAHs: ●, adamantane ($C_{10}H_{16}$); ○, naphthalene ($C_{10}H_8$);[12] ■, diamantane ($C_{14}H_{20}$); □, anthracene ($C_{14}H_{10}$);[12] Δ, phenanthrene ($C_{14}H_{10}$).[24] The lines show the best fits of the data with eq 1.

Table 2. Least-Squares Estimates of the Coefficients a_1, a_2, and a_3 of Equation 1 and the Standard Deviations (SD) of the Estimates, with $T_{\min}$ and $T_{\max}$ Indicating the Minimum and the Maximum Temperatures of the Solubility Measurements, Respectively

solute	adamantane	diamantane
$T_{\min}$/K	313.2	313.2
$T_{\max}$/K	493.2	493.2
a_1	−51.89	−26.50
SD a_1	4.55	6.17
a_2	33.79	4.353
SD a_2	4.66	6.31
a_3	45.44	27.37
SD a_3	3.55	4.81

the measured solubility was carried out with adamantane at 333.2 K and 5 MPa using fused-silica restrictors of various lengths and diameters. The results of the test did not indicate any significant variation in the composition of the aqueous effluent as the flow rate of water varied within (0.007 to 0.027) $\mathrm{g \cdot s^{-1}}$. The standard uncertainty[25] in the measurement of the extraction cell temperature was ± 0.10 K, and the standard uncertainty in the measurement of pressure was ± 0.1 MPa. The previous applications of the apparatus to measure the aqueous solubilities of solid aromatics[12,14,24] showed a good agreement with literature data.

GC/MS Operating Conditions. A TraceGC gas chromatograph fitted with a TriPlus AS autosampler was equipped with a DB-5 capillary column (30 m × 0.25 mm i.d., polymer film thickness 0.25 μm, J&W Scientific, Folsom, CA) and coupled to a PolarisQ mass spectrometer (TraceGC + PolarisQ, Thermo Finnigan, San Jose, CA). The carrier gas was helium (99.995 %, SIAD, Braňany u Mostu, Czech Republic), and the ionization energy (EI mode) was 70 eV. The techniques of injection into GC differed between the two solutes. In diamantane, splitless injection was employed which was the technique used in our previous studies with other solutes. In the measurements with adamantane, however, splitless injection resulted in poor peak shape so that split injection was employed in adamantane to improve the peak shape and increase the run-to-run reproducibility. In the adamantane runs, the GC oven temperature was programmed from 323 K (6 s) at $0.17\ \mathrm{K \cdot s^{-1}}$ to 423 K (6 s). In diamantane, the temperature program was the same except for the final temperature of 463 K.

Results and Discussion

Solubility Data. The aqueous solubilities (equilibrium mole fractions, x_2) of adamantane and diamantane are listed in Table 1. We are not aware of any previous literature report of aqueous solubility of either adamantane or diamantane. Therefore, there seems to be no independent experimental information to assess the accuracy of the present results. Instead, the solubilities of diamondoids will be compared with those of PAHs of the same carbon numbers. Figure 1 shows that, depending on temperature, the aqueous solubility of adamantane is lower than that of naphthalene by a factor of 240 to 400. The solubility of diamantane is 9- to 17-times lower than that of anthracene and 170- to 260-times lower than that of phenanthrene. These data confirm the expectation that solubility of a diamondoid should be lower than solubility of an aromatic hydrocarbon of the same carbon number. The apparent similarity between the aqueous solubilities of adamantane ($C_{10}H_{16}$) and anthracene ($C_{14}H_{10}$) results from a fortuitous tradeoff between the solute−water interactions and the pure-solute properties.

The present measurements with diamondoids proved to be more difficult than our previous studies with PAHs and aromatic heterocycles. Compared with the previous solutes, the diamondoids tended to a more rapid nucleation and precipitation from the aqueous solution, and this effect gained in importance as the operating temperature increased. The solute nucleation within the fused silica restrictor did not affect the results provided that the solute particles were transported by the flowing solution to the collecting vial. At high operating temperatures, however, the outlet end of the restrictor easily became clogged with the precipitating solute. For this reason, in diamondoids, the temperature ranges of the measurements did not extend all the way to the solid–liquid–vapor triple-point temperatures of the solutes. Considering the data in Table 1 and the standard uncertainties in temperature and pressure mentioned above, we conclude that the relative expanded uncertainty[25] in the resultant solubilities is ± 13 % (confidence level of 95 %).

Variation of Solubility with Temperature. As indicated by simple linear fits of the data from Table 1, the mean values of the relative increase in solubility with temperature, $(\partial \ln x_2/\partial T)_\sigma$, are $0.050\ \mathrm{K^{-1}}$ and $0.060\ \mathrm{K^{-1}}$ in adamantane and diamantane, respectively. These values are comparable to those reported before for PAHs, namely, $0.054\ \mathrm{K^{-1}}$, $0.058\ \mathrm{K^{-1}}$, and $0.054\ \mathrm{K^{-1}}$ in naphthalene,[12] anthracene,[12] and phenanthrene,[24]

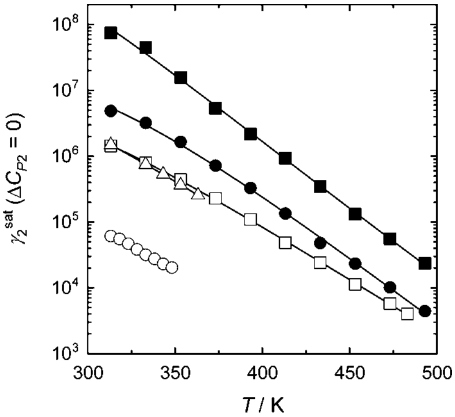

Figure 2. Estimates of activity coefficients of diamondoids and selected PAHs in saturated aqueous solutions (ΔC_{P2}/J·mol^{-1}·K^{-1} = 0): ●, adamantane ($C_{10}H_{16}$); ○, naphthalene ($C_{10}H_8$);[13] ■, diamantane ($C_{14}H_{20}$); □, anthracene ($C_{14}H_{10}$);[13] Δ, phenanthrene ($C_{14}H_{10}$).[24] The lines serve just to guide the eye.

respectively. A more detailed insight results from fitting the solubility data from Table 1 with

$$\ln x_2 = a_1 + a_2(T_0/T) + a_3 \ln(T/T_0) \tag{1}$$

where $T_0 = 298.15$ K. Table 2 shows the least-squares estimates of the coefficients a_1, a_2, and a_3. The ratio of a coefficient estimate to the standard deviation of the coefficient estimate can be compared to the pertinent critical values of the Student's *t* distribution[26] to test the hypothesis "the coefficient equals zero". In all coefficients except a_2 of diamantane, the hypothesis is rejected at a confidence level of 98 %, indicating that most coefficients are statistically significant.

Estimation of Activity Coefficients. The solubility x_2 of a solid solute (2) in a liquid solvent (1) is given by

$$x_2 = \frac{f_2^{\mathrm{s0}}}{\gamma_2^{\mathrm{sat}} f_2^{\mathrm{l0}}} \tag{2}$$

where f_2^{s0} and f_2^{l0} are the fugacities of the pure solid solute and the pure subcooled liquid solute, respectively, and γ_2^{sat} is the Raoult-law activity coefficient of the solute in the saturated solution. The activity coefficient is referred to the pure subcooled liquid solute at the particular temperature and pressure. Equation 2 applies if the solid phase in equilibrium with the solution is pure solute. The fugacity ratio in eq 2 can be obtained from the thermochemical cycle described by Prausnitz et al.[27]

$$\ln \frac{f_2^{\mathrm{s0}}}{f_2^{\mathrm{l0}}} = \frac{\Delta H_2^{\mathrm{fus}}}{RT_{\mathrm{t2}}}\left(1 - \frac{T_{\mathrm{t2}}}{T}\right) + \frac{\Delta C_{P2}}{R}\left(\frac{T_{\mathrm{t2}}}{T} - 1\right) - \frac{\Delta C_{P2}}{R} \ln \frac{T_{\mathrm{t2}}}{T} + \frac{(V_2^{\mathrm{s0}} - V_2^{\mathrm{l0}})P}{RT} \tag{3}$$

where *R* is the molar gas constant; *T* is the temperature; T_{t2} is the triple-point temperature of the solute; $\Delta H_2^{\mathrm{fus}}$ is the molar enthalpy of fusion of the solute at T_{t2}; ΔC_{P2} is the difference between the molar isobaric heat capacities of the pure subcooled liquid solute and the pure solid solute ($= C_{p2}^{\mathrm{l0}} - C_{p2}^{\mathrm{s0}}$); and V_2^{s0} and V_2^{l0} are the molar volumes of the pure solid solute and the pure subcooled liquid solute, respectively. The last term on the rhs of eq 3 accounts for the effect of elevated pressure on f_2^{s0} and f_2^{l0} assuming that both the solid solute and the subcooled liquid solute are incompressible and that their respective vapor pressures are negligible with respect to the total pressure *P*.

Equation 3 applies only if there are no solid–solid phase transitions in the pure solute within the temperature interval from *T* to T_{t2}. With regard to the present solutes, this is the case of adamantane because a solid–solid phase transition reported[28] in adamantane occurs at 208.62 K, i.e., far below the temperature range of our measurements. In diamantane, however, there are two solid–solid phase transitions,[29] one at transition temperature T_{transA} = 440.43 K with transition enthalpy $\Delta H_2^{\mathrm{transA}}$ = 8960 J·mol^{-1} and another at T_{transB} = 407.22 K with $\Delta H_2^{\mathrm{transB}}$ = 4445 J·mol^{-1}. To account for the phase transitions in the pure solid diamantane, eq 3 can be modified as

$$\ln\left(\frac{f_2^{\mathrm{s0}}}{f_2^{\mathrm{l0}}}\right) = \frac{\Delta H_2^{\mathrm{fus}}}{RT_{\mathrm{t2}}}\left(1 - \frac{T_{\mathrm{t2}}}{T}\right) + \frac{\Delta H_2^{\mathrm{transA}}}{RT_{\mathrm{transA}}}\left(1 - \frac{T_{\mathrm{transA}}}{T}\right) + \frac{\Delta H_2^{\mathrm{transB}}}{RT_{\mathrm{transB}}}\left(1 - \frac{T_{\mathrm{transB}}}{T}\right) + \frac{\Delta C_{P2}}{R}\left(\frac{T_{\mathrm{t2}}}{T} - 1 - \ln \frac{T_{\mathrm{t2}}}{T}\right) + \frac{(V_2^{\mathrm{s0}} - V_2^{\mathrm{l0}})P}{RT} \tag{4}$$

where a particular solid–solid phase transition term is included only if the respective transition temperature exceeds the operating temperature *T*.

Equations 3 and 4 together with eq 1 were employed for x_2-to-γ_2^{sat} conversions in adamantane and diamantane, respectively. The triple-point temperature and enthalpy of fusion data of adamantane were 541.7 K[19] and 12430 J·mol^{-1},[30] respectively. In diamantane, the data were T_{t2} = 517.65 K[19] and $\Delta H_2^{\mathrm{fus}}$ = 8646 J·mol^{-1}.[29] The molar volumes of subcooled liquid solutes were evaluated from the modified Rackett equation[31] using the critical temperatures and critical pressures estimated from the Joback correlation.[32,33] The molar volumes of solid solutes were obtained using the correlation of Goodman et al.[34]

To the best of our knowledge, no experimental data on ΔC_{P2} are available in either adamantane or diamantane. Therefore, the activity coefficients of diamondoids in saturated aqueous solutions were estimated employing two common approximations[35] of ΔC_{P2}, namely, ΔC_{P2}/J·mol^{-1}·K^{-1} = 0 and $\Delta C_{P2} = \Delta S_2^{\mathrm{fus}}$, where $\Delta S_2^{\mathrm{fus}}$ is the entropy of fusion. In adamantane, a value of $\Delta S_2^{\mathrm{fus}}$ = 22.95 J·mol^{-1}·K^{-1} was estimated from the T_{t2} and $\Delta H_2^{\mathrm{fus}}$ data mentioned above, whereas an experimental value[29] of $\Delta S_2^{\mathrm{fus}}$ = 16.79 J·mol^{-1}·K^{-1} was used in diamantane.

Activity Coefficients: Diamondoids vs PAHs. Figure 2 shows the activity coefficients of the two diamondoids and selected PAHs in saturated aqueous solutions. The data plotted in Figure 2 were calculated assuming ΔC_{P2}/J·mol^{-1}·K^{-1} = 0. Because of the logarithmic scale of the vertical axis, the plot obtained with $\Delta C_{P2} = \Delta S_2^{\mathrm{fus}}$ would be very similar to Figure 2 and is not shown here. However, the numerical values of the activity coefficients of diamondoids as obtained with either approximation of ΔC_{P2} are available in the Supporting Information file.

Figure 2 confirms the expectation that a diamondoid molecule should be more hydrophobic as compared with a PAH molecule with the same carbon number. Depending on temperature and on the particular approximation of ΔC_{P2}, the activity coefficient of adamantane in saturated aqueous solution exceeds that of naphthalene by a factor ranging within 70 to 150, whereas the activity coefficient of diamantane in saturated aqueous solution exceeds that of anthracene by a factor ranging within 10 to 50. Figure 2 shows that, at a particular temperature, the adamantane–naphthalene factor is always larger than the diamantane–anthracene factor. The difference perhaps results from the molecular geometries because, in diamantane, the tertiary carbon atoms at the fusion of cages can experience some steric hindrance from interaction with water molecules. If this were the case, the hydrophobic nature of the particular atoms/groups would not manifest itself to the full extent in the interaction with water molecules.

Conclusion

A dynamic method with a flow-through extraction cell was employed to measure the solubilities of adamantane and diamantane at temperatures between 313 K and the solid–liquid–vapor triple-point temperature of the solute. The aqueous solubility of adamantane is 240- to 400-times lower than that of naphthalene at the particular temperature, whereas the aqueous solubility of diamantane is 9- to 17-times lower than that of anthracene at the particular temperature.

Supporting Information Available:

Estimates of the activity coefficients of diamondoids in aqueous solutions. The estimates were obtained assuming $\Delta C_{P2}/\mathrm{J \cdot mol^{-1} \cdot K^{-1}} = 0$ (Table S1) or $\Delta C_{P2} = \Delta S_2^{\mathrm{fus}}$ (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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