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Solubility of Diamantane, Trimantane, Tetramantane, and Their Derivatives in Organic Solvents

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The solubility of diamantane, trimantane, tetramantane, and their derivatives in acetone, cyclohexane, ethyl acetate, toluene, heptane, and 1-pentanol was measured using the solid disappearance method for temperatures ranging from (273.15 to 348.15) K. The experimental solubility data have been correlated with different thermodynamic models to obtain engineering parameters for use in process design.

Introduction

Diamondoids are a class of thermodynamically stable, saturated hydrocarbons consisting of fused cyclohexane rings in the form of a “cagelike” structure. Thus, adamantane ($C_{10}H_{16}$), diamantane ($C_{14}H_{20}$), trimantane ($C_{18}H_{24}$), and tetramantane ($C_{22}H_{28}$) contain one, two, three, and four such cages, respectively (Figure 1). There is only one form of adamantane, diamantane, and trimantane, but there are four tetramantane isomers. The higher diamondoids exhibit increasing structural complexity and molecular geometrical varieties.

Synthesis of diamondoids is possible but difficult. Indeed, the synthesis of diamondoids with more than four cages has so far been futile. However, diamondoids occur naturally in petroleum and have been used as indicators of natural oil cracking.[1] With a combination of distillation, pyrolysis, chromatography, and crystallization, diamondoids with up to 11 cages have been isolated and crystallized from petroleum.[2,3] In addition, derivatives have been formed by attaching various groups such as bromo, hydroxyl, and amino to such diamondoids.

With their unique yet stable and diverse molecular structures, diamondoids as well as their derivatives have the potential of enabling a new generation of novel and durable nanotechnology devices and materials. For commercial applications, it is crucial that large quantities of diamondoids of different degrees of purity be available at a reasonable cost. Experience shows that crystallization or crystallization−chromatography hybrids have a role to play if cost reduction can be realized.[4,5] Solubility data are indispensable in the design of crystallization-based separation processes to recover the diamondoids from petroleum.[6,7] This paper reports the solubility data of diamantane, trimantane, tetramantane, and their derivatives in various organic solvents as measured by a solid disappearance method. The data can be used for the selection of suitable solvents for the synthesis of extraction/crystallization processes for the recovery and separation of diamondoids.

Experimental Section

Materials. Three diamondoids, namely, diamantane ($w > 0.995$), trimantane ($w > 0.99$), and tetramantane ($w > 0.99$), and two diamantane derivatives, namely, 1-hydroxyl diamantane and 1,6-dihydroxyl diamantane, were supplied by the Chevron Corporation. The solubilities were measured in seven organic solvents: acetone (HPLC, > 99.8 %, Fisher), cyclohexane (HPLC, > 99.95 %, Aldrich), ethyl acetate (HPLC, > 99.95 %, Acros), toluene (HPLC, > 99.8 %, Fisher), heptane (HPLC, > 99.0 %, Fisher), 1-pentanol (HPLC, > 99.0 %, Fisher), and methanol (HPLC, > 99.0 %, Fisher). All solvents were used without further purification.

Solubility Measurement. An amount of the compound in excess of the expected solubility at the measurement temperature was weighed with an electronic balance (OHAUS, Explorer Pro, accuracy ± 0.1 mg) and introduced to a 30 mL jacketed glass

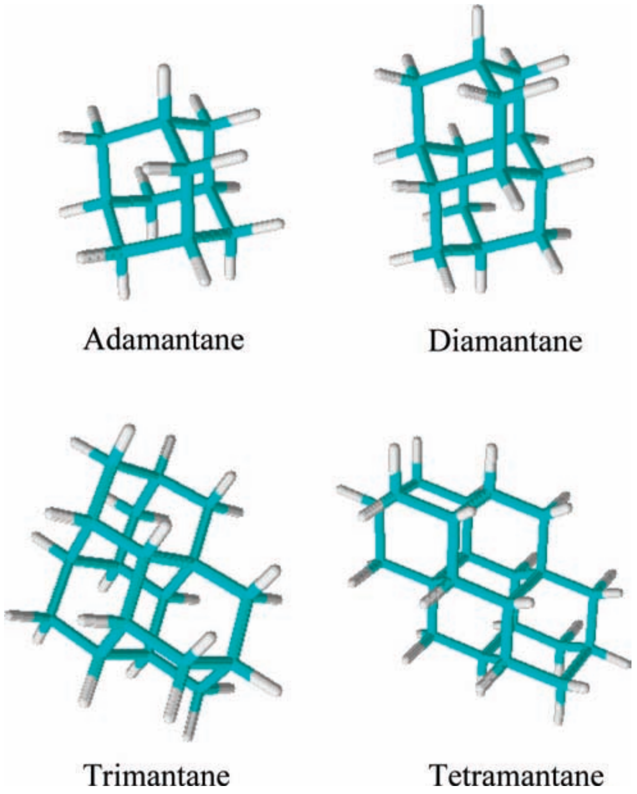

Figure 1. Molecular structures of diamondoids.

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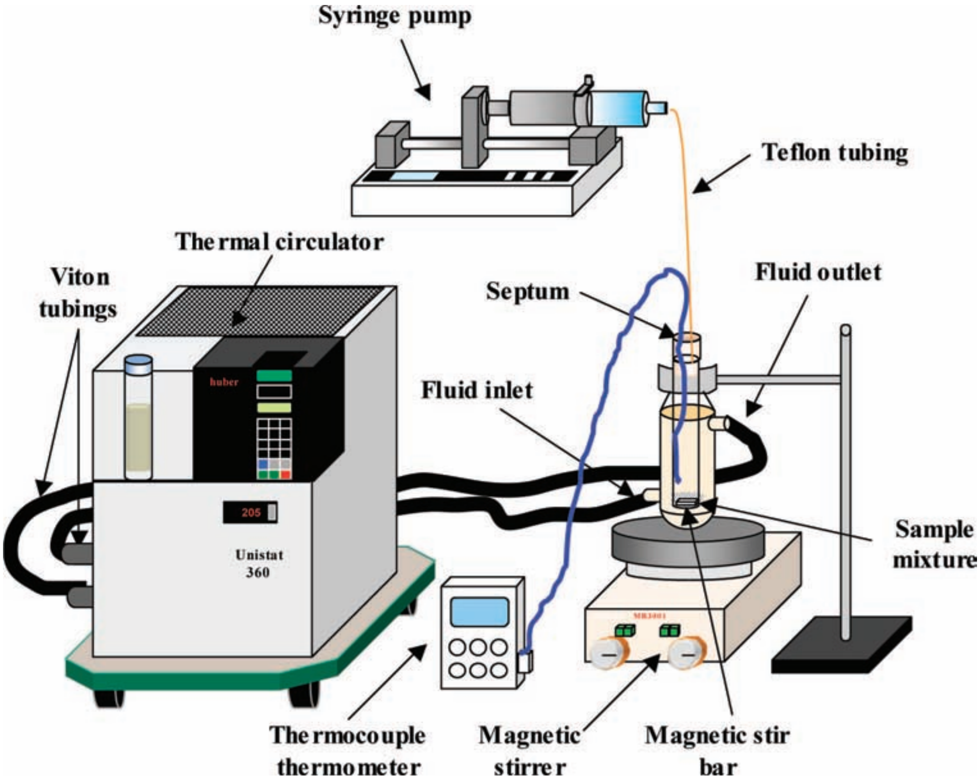

Figure 2. Schematic diagram of the experimental setup for solubility measurements.

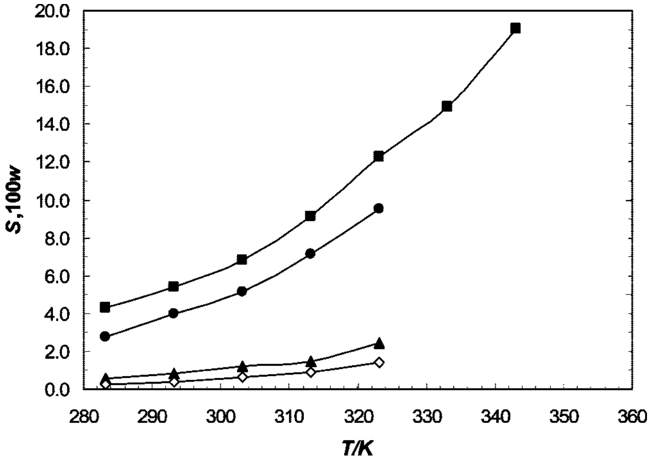

Figure 3. Mass fraction solubility, *S*, of diamantane in ◇, acetone; ▲, ethyl acetate; ●, toluene; ■, cyclohexane at various temperatures.

vessel. The selected solvent was added to the vessel with a gastight syringe (Hamilton, 1750RN, 500 μL). The vessel was sealed with a PTFE septum and PTFE tape to minimize the loss of solvent to the atmosphere due to evaporation. The vessel was then connected to an oil circulation bath (Huber, Minstat cc2) that was set at the required temperature. Stirring of the mixture was provided by a magnetic bar. The temperatures were read with an accuracy of ± 0.1 K with a thermometer (Cole Parmer, Digi-Sense). The experimental setup is depicted in Figure 2.

The solution was heated to 10 K below the boiling temperature of the solvent to dissolve all the solids and obtain a homogeneous solution. The homogeneous solution was then cooled at a rate of 1 $\mathrm{K \cdot min^{-1}}$ to the measurement temperature to recrystallize the compound. The solid−liquid mixture was equilibrated at the measurement temperature for 30 min. This was followed by gradually adding the solvent from the syringe to dissolve all the remaining solids at the same temperature. The total amount of solvent added was recorded. Additional details of this solid disappearance method can be found in Kwok et al.[8] The measurements covered the temperature range from (273.15 to 348.15) K. Uncertainty in the solubility data originated from the weighing of the solute and solvent. An error analysis showed that the uncertainty in solubility was about ± 1 %. The uncertainty in temperature for each data point was ± 0.1 K.

Results and Discussion

Diamantane, Trimantane, and Tetramantane. The solubility of diamantane decreases in the order of cyclohexane, toluene, ethyl acetate, and acetone (Figure 3). The observed trend is mainly related to the increasing polarity of the solvents, since diamantane is nonpolar in nature. The continuity of the diamantane solubility curves shows the absence of solvates in these systems. The solubility of trimantane shows a similar trend with a higher solubility in nonpolar solvents (cyclohexane, toluene, and heptane) than in polar solvents (1-pentanol and ethyl acetate) (Figure 4). Interestingly, the solubility of tetramantane in cyclohexane is below the solubility in toluene and heptane, although the solubility in polar solvents is still lower than those in nonpolar solvents (Figure 5). A summary of the solubility data of diamantane, trimantane, and tetramantane is presented in Table 1.

Solubility of Diamondoids in Cyclohexane. The solubility of diamantane, trimantane, and tetramantane in cyclohexane is plotted in Figure 6. It shows that the solubility of trimantane is higher than that of diamantane in the range of temperatures studied, giving a reversal in solubility with an increase in molecular size. No explanation for this reversal can be offered at this time. As expected, tetramantane with a higher molecular weight shows the lowest solubility.

Diamantane Derivatives. The solubility of 1-hydroxyl diamantane and 1,6-dihydroxyl diamantane in pure methanol and

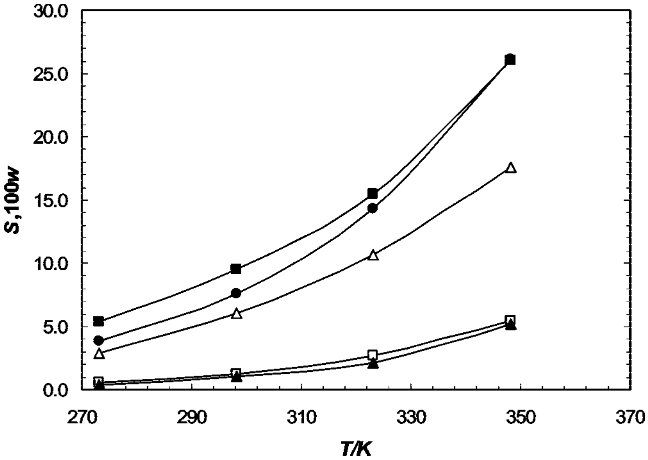

Figure 4. Mass fraction solubility, *S*, of trimantane in ▲, ethyl acetate; ●, toluene; ■, cyclohexane; △, hetpane; □, 1-pentanol at various temperatures.

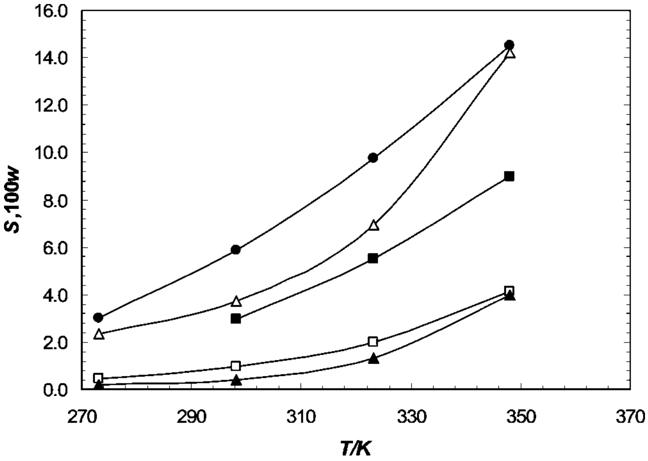

Figure 5. Mass fraction solubilities, *S*, of tetramantane in ▲, ethyl acetate; ●, toluene; ■, cyclohexane; △, hetpane; □, 1-pentanol at various temperatures.

Table 1. Experimental Mass Fraction Solubility, *S*, of Diamantane, Trimantane, and Tetramantane in Cyclohexane, Ethyl Acetate, Toluene, Acetone, Heptane, and 1-Pentanol as a Function of Temperature *T*

	100 *w*					
T/K	cyclohexane	ethyl acetate	toluene	acetone	heptane	1-pentanol
			Diamantane			
283.15	4.336	0.555	2.790	0.274		
293.15	5.430	0.820	3.976	0.412		
303.15	6.827	1.191	5.132	0.633		
313.15	9.144	1.495	7.148	0.905		
323.15	12.259	2.413	9.520	1.425		
333.15	14.945					
343.15	19.022					
			Trimantane			
273.15	5.396	0.396	3.802		2.842	0.600
298.15	9.553	1.010	7.642		6.503	1.272
323.15	15.492	2.120	14.314		10.651	2.725
348.15	26.012	5.175	26.152		17.564	5.436
			Tetramantane			
273.15		0.216	3.032		2.360	0.474
298.15	2.968	0.412	5.885		3.733	0.958
323.15	5.517	1.327	9.748		6.942	2.006
348.15	8.992	3.980	14.511		14.219	4.118

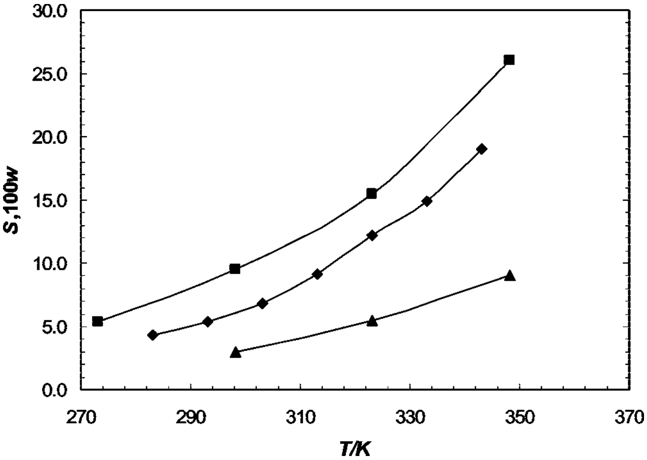

Figure 6. Comparison for mass fraction solubilities, *S*, of □, diamantane; ■, trimantane; and ▲, tetramantane in cyclohexane at various temperatures.

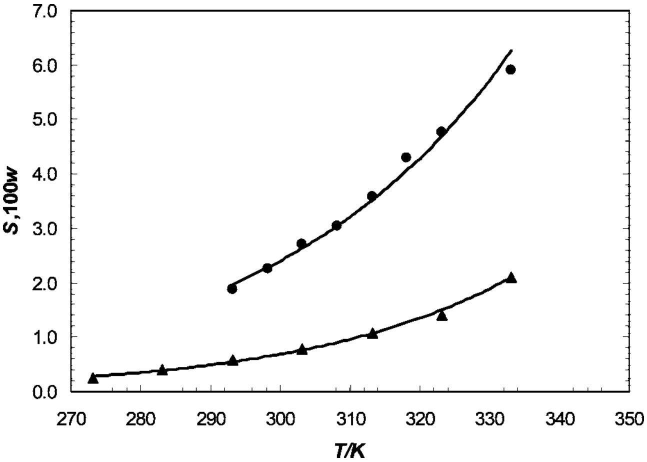

Figure 7. Mass fraction solubility, *S*, of 1-hydroxyl diamantane in ●, methanol ($w = 0.99$); ▲, aqueous methanol ($w = 0.80$) at various temperatures.

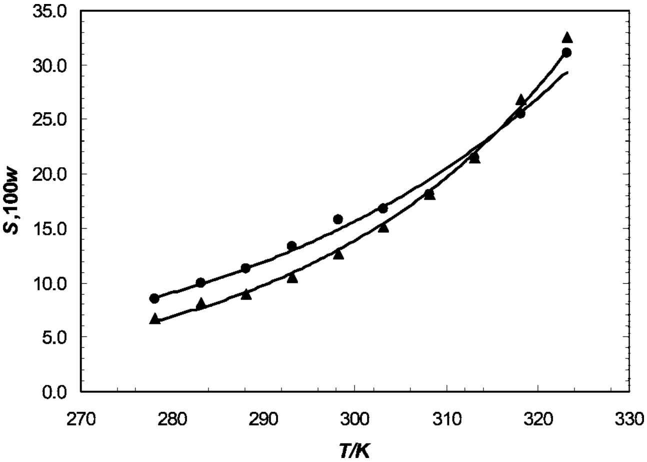

Figure 8. Mass fraction solubility, *S*, of 1,6-dihydroxyl diamantane in ●, methanol ($w = 0.99$); ▲, aqueous methanol ($w = 0.80$) at various temperatures.

an aqueous methanol solution ($w = 0.80$) is shown in Figures 7 and 8, respectively. The solubility data are given in Table 2. The addition of hydroxyl group(s) greatly enhances the solubility of both derivatives in polar solvents. As expected, 1-hydroxyl diamantane has significantly lower solubility than 1,6-dihydroxyl diamantane within the temperature range investigated. Water has a considerable influence on 1-hydroxyl diamantane solubility, while the effect on 1,6-dihydroxyl diamantane with two hydroxyl groups is minimal. It is observed that the rate of change of solubility as a function of temperature of 1,6-dihydroxyl

Table 2. Experimental Mass Fraction Solubility, *S*, of 1-Hydroxyl Diamantane and 1,6-Dihydroxyl Diamantane in Methanol (1) + Water (2) Solvent Mixtures As a Function of Temperature *T*

	100 w			
	1-hydroxyl diamantane		1,6-dihydroxyl diamantane	
T/K	$w_1 = 1.00$	$w_1 = 0.80$	$w_1 = 1.00$	$w_1 = 0.80$
273.15		0.254		
278.15			8.553	6.672
283.15		0.407	9.937	8.114
288.15			11.283	8.942
293.15	1.885	0.580	13.282	10.551
298.15	2.257		15.728	12.611
303.15	2.709	0.791	16.810	15.041
308.15	3.042		18.148	18.132
313.15	3.581	1.072	21.493	21.512
318.15	4.305		25.519	26.848
323.15	4.759	1.415	25.519	32.578
333.15	5.900	2.111		

Table 3. NRTL Model Parameters of Equation 2 and Equation 3 for Diamantane in Various Solvents in the Temperature Range from (283.15 to 323.15) K

	τ_{12}	τ_{21}	α_{12}
cyclohexane	2.5178	55.8068	0.5468
ethyl acetate	4.5062	94.6302	0.6237
toluene	2.9294	49.4900	0.6022
acetone	5.0941	1.3875	0.7376

diamantane in aqueous methanol ($w = 0.8$) is faster than that in methanol. The fact that the solubility curves cross each other seems to indicate the increasing influence of water on the solubility of 1,6-dihydroxyl diamantane at higher temperatures.

Correlation by the NRTL Model. The measured solubilities of diamantane in acetone, cyclohexane, ethyl acetate, and toluene were correlated using the solubility equation

$$\ln(\gamma_2 x_2) = -\frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{m}}}\right) \tag{1}$$

and an activity coefficient model such as the NRTL model

$$\ln(\gamma_2) = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2 G_{21})^2}\right] \tag{2}$$

where

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \text{ and } G_{21} = \exp(-\alpha_{12}\tau_{21}) \tag{3}$$

Here, γ_2 is the activity coefficient of diamantane and x_1 and x_2 are the mole fraction of solvent and diamantane, respectively. The melting temperature, T_{m}, and the heat of fusion, $\Delta_{\text{fus}}H$, of diamantane are 509.65 K and 9204.8 J·mol^{-1}, respectively.[9]

The interaction parameters, τ_{12} and τ_{21} in eq 2 and α_{12} in eq 3, were determined by regression of the experimental solubility data of diamantane in the corresponding solvent by the minimization of the following function at each temperature

$$\min F = \sum_{i=1}^{n}\left(\frac{\gamma_{i,\text{exptl}} - \gamma_{i,\text{NRTL}}}{\gamma_{i,\text{exptl}}}\right)^2 \tag{4}$$

Here, $\gamma_{2,\text{NRTL}}$ is the activity coefficient calculated using eq 2, whereas $\gamma_{2,\text{exptl}}$ is that calculated by using the experimental solubility data in eq 1. The values of the model parameters of eq 2 and eq 3 are listed in Table 3. A comparison of the solubility curves in acetone, cyclohexane, ethyl acetate, and toluene as predicted using these model parameters and the actual experimental data points shows excellent agreement (Figure 9).

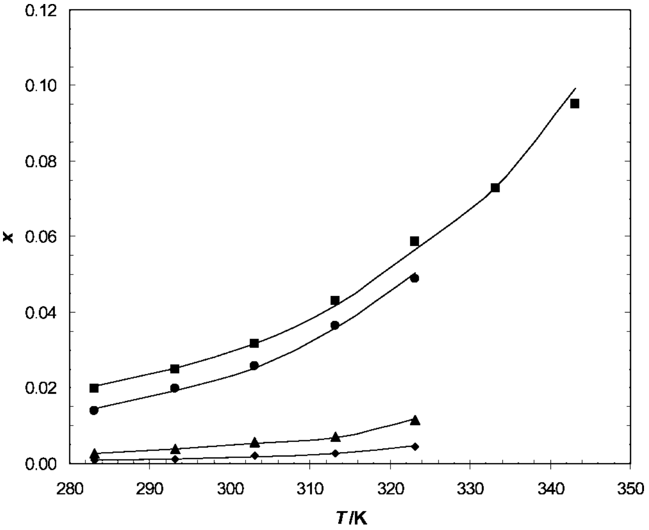

Figure 9. Mole fraction solubility, x, of diamantane in ◆, acetone; ▲, ethyl acetate; ●, toluene; ■, cyclohexane at various temperatures; — solid curves, calculated from the NRTL model.

Table 4. Parameters of Equation 5 for Trimantane, Tetramantane, 1-Hydroxyl Diamantane, and 1,6-Dihydroxyl Diamantane in Various Solvents in the Temperature Range from (273.15 to 348.15) K

solvent	A	B	C	rmsd
		Trimantane		
cyclohexane	−18.2864	757.9048	2.7692	0.0064
ethyl acetate	−0.3193	0.9755	0.0565	0.0029
heptane	−4.8303	166.2291	0.7543	0.0043
1-pentanol	−0.3376	0.9751	0.0599	0.0025
toluene	−21.8978	902.3017	3.3170	0.0031
		Tetramantane		
cyclohexane	−64.4855	−0.3993	11.4693	0.1061
ethyl acetate	−19.1706	0.5681	3.4276	0.2261
heptane	−67.7475	−0.5003	12.1924	0.6396
1-pentanol	−19.3400	0.5606	3.4703	0.1609
toluene	−75.8701	−0.6888	13.6783	0.2908
		1-Hydroxyl Diamantane		
methanol	−0.2969	0.9616	0.0522	0.0003
aqueous methanol (w= 0.8)	−0.0687	0.7752	0.0118	0.0003
		1,6-Dihydroxyl Diamantane		
methanol	−1.6982	0.9452	0.3023	0.0048
aqueous methanol (w= 0.8)	−1.6318	6.2926	0.2863	0.0061

Correlation by Empirical Model. Since the melting temperatures and enthalpies of fusion of other diamondoids, other than diamantane, and their derivatives are unknown, the solubility data are correlated by the following empirical model

$$\ln x = A + \frac{B}{T/\text{K}} + C\ln(T/\text{K}) \tag{5}$$

The parameters A, B, and C were evaluated using nonlinear optimization from excel solver and presented in Table 4 together with the root-mean-square deviations (rmsd)

$$\text{rmsd} = \left[\sum_{i=1}^{N}\frac{x_{i,\text{c}} - x_{i,\text{exptl}}}{N}\right]^{1/2} \tag{6}$$

where N is the number of experimental data points and $x_{i,\text{exptl}}$ and $x_{i,\text{c}}$ refer to the experimental solubility and solubility calculated from eq 5, respectively. The results show that the empirical equation can be used to correlate satisfactorily the solubility of trimantane, tetramantane, 1-hydroxyl diamantane, and 1,6-dihydroxyl diamantane.

Conclusions

Solubilities of diamantane, trimantane, tetramantane, 1-hydroxyl diamantane, and 1,6-dihydroxyl diamantane in various organic solvents were determined at different temperatures. The solubility of the saturated diamondoids is higher in nonpolar solvents than polar solvents. The dependence on molecular size is not obvious perhaps because the difference in size of the three diamonds is not sufficiently significant. With the exception of tetramantane, both diamantane and trimantane exhibit a higher solubility in cyclohexane than in toluene. Note that the solubility for tetramantane represents the collective outcome of four tetramantane isomers since no attempt was made to separate them for this study. 1-Hydroxyl diamantane and 1,6-dihydroxyl diamantane exhibit high solubility in polar solvents. The solubility of diamondoids and their derivatives reveals some of the characteristics of this class of compounds which can be exploited for process design. Further effort along this direction is underway.

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