

Solubility of Docosane in Heptane

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The solubility of docosane in heptane has been determined in the range of (277.25–317.65) K. The effect of ultrasonic waves in the solubility was studied. The results can be fitted with high accuracy to the relationship $\log_{10}(x_1) = A + B/T + C \log_{10}(T)$. It was found out that the ultrasound did not affect the system solubility and the system behaved as an ideal solution.

Introduction

Solubility data for a solute–solvent system are the starting point to determine or estimate other crystallization parameters, such as crystal nucleation and growth.

Few data of solubility of long-chain paraffins in alkanes of low molecular weight are available in the literature.^{1–5} These data are relevant to the petroleum chemistry field, and they are also necessary to crystallization kinetics study.

The solubility of a long-chain hydrocarbon in an organic solvent depends not only on the hydrocarbon chain length and the solvent molecular structure but also on the attractive forces between these molecules. Therefore, it is very difficult to predict if the system will behave as an ideal or nonideal mixture.

The use of ultrasound technology in commercial applications has been increasing significantly in recent years. There is evidence that ultrasound can influence various chemical processes, including crystallization.^{1,2,6–8}

Experimental Procedure

Materials. The solvent was heptane purchased from Anidrol Prods. Químicos Ltd. with a stated boiling point of 371.45 K. The docosane (*n*-alkane C₂₂), melting point 316.9 K, was purchased from Alfa Aesar (Johnson Matthey Co.). The purity of both substances was 99 mol %; therefore, they were used without further purification.

Method of Measurement. Solutions of docosane in heptane of known concentration were prepared by mass; pure components were placed in an appropriate crystallizing apparatus (Figure 1), comprising an 80 cm³ glass reactor with an outer jacket, through which a mixture of water and ethylene glycol from a thermostat was circulated, a glass four-blade stirrer (500 rpm), and two ultrasonic cleaning baths filled with water. One of the baths operated with a frequency of 25 kHz and a 50 W power supply, and the other operated with a frequency of 40 kHz and a 30 W power supply. The glass reactor was closed to

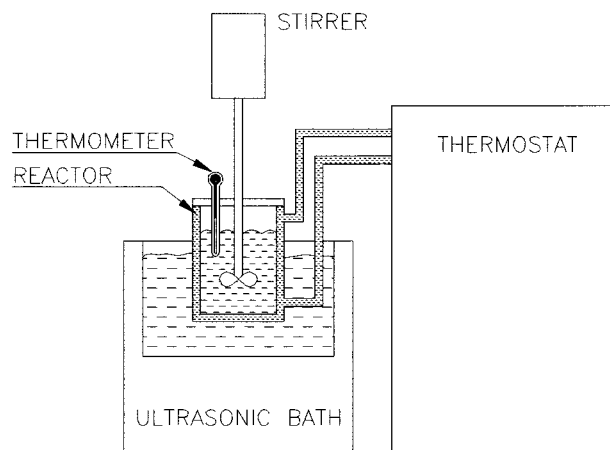


Figure 1. Experimental apparatus.

prevent the solvent evaporation, and it was maintained submerged in the ultrasonic bath. The temperature of the solution was continuously recorded using a mercury thermometer with an accuracy of ± 0.05 K.

The solubility was determined according to Nývlt's methodology,⁹ by which the solution was preheated until all crystals were dissolved, then the solution was cooled slowly at three different constant rates of (6.0, 18.0, and 30.0) K/h to a temperature at which a sufficient number of tiny crystals were formed, and, finally, the temperature was slowly raised at the rate of 0.6 K/h until the last crystal was dissolved. This temperature was considered to be the saturation temperature of solution, T_{eq} . The temperature could be determined with considerable precision by careful observation through magnifying glasses when the solution was illuminated with a powerful light at right angles to the observation axis. The procedure was repeated three times for each cooling rate. The deviation during reproducibility of experiments was just about 0.1 K.^{1,2,9–11}

The effect of ultrasonic waves on the solubility of docosane in heptane was also determined. The experiments were carried out in the same form. The ultrasonic generator was allowed to operate continuously during the experiments.

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Table 1. UNIFAC Parameters

group	subgroup	<i>R</i>	<i>Q</i>
(1) CH ₂	(1) CH ₃ –	0.9011	0.848
(1) CH ₂	(2) –CH ₂ –	0.6744	0.540

Prediction

The solubility of any solid substance in an ideal system at constant pressure follows the relationship^{4,5,12}

$$\ln x_1 = \frac{\Delta H_{f1}}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) \quad (1)$$

where ΔH_{f1} is the enthalpy of fusion of the solute at its melting point (T_m) and x_1 is the solute mole fraction.

For the substances with a first-order transition point we have, for $T < T_{tr}$ ^{5,6,12}

$$\ln x_1 = \frac{\Delta H_{f1}}{R} \left(\frac{1}{T_m} - \frac{1}{T_{tr}} \right) + \frac{\Delta H_{f1} + \Delta H_{tr1}}{R} \left(\frac{1}{T_{tr}} - \frac{1}{T} \right) \quad (2)$$

where ΔH_{tr1} is the enthalpy on transition of the solid and T_{tr} is the pure solid transition temperature.

For a nonideal system, eq 3 provides a reasonable method for predicting the saturation mole fraction of a solid in a liquid:^{3,4,12}

$$\ln \gamma_1 x_1 = -\frac{\Delta H_{f1}}{RT_m} \left(\frac{T_m}{T} - 1 \right) + \frac{\Delta C_{p1}}{R} \left[\ln \left(\frac{T}{T_m} \right) + \frac{T_m}{T} - 1 \right] \quad (3)$$

In eq 3 γ_1 is the liquid-phase activity coefficient of the solute and ΔC_{p1} is the change of the heat capacity of the pure solute on fusion ($\Delta C_{p1} = \Delta C_{p1}(\text{liquid}) - \Delta C_{p1}(\text{solid})$).

For an ideal system, eq 3 could be used with the parameter γ_1 equal to 1.

When a phase transition takes place between T and T_m , eq 3 should be modified to include the effect of the transition point:^{3–5}

$$\ln \gamma_1 x_1 = -\frac{\Delta H_{f1}}{RT_m} \left(\frac{T_m}{T} - 1 \right) - \frac{\Delta C_{p1}}{R} \left[\ln \left(\frac{T_m}{T} \right) \right] + \frac{\Delta C_{p1}}{R} \left[\frac{T_m}{T} - 1 \right] + \frac{\Delta H_{tr1}}{RT_{tr}} \left(\frac{T_{tr}}{T} - 1 \right) \quad (4)$$

UNIFAC Method^{4,13,14} This is based on the assumption that a physical property of a compound is the sum of contributions made by all of the functional groups in the molecule. The molecular activity coefficient is separated into two parts, combinatorial and residual. The former is due to differences in the shape and size of the molecules in the mixture, whereas the latter arises from interactions between structural groups. Both sizes of the functional groups and the interaction areas are taken from pure component molecular structure data. The program used in this paper was UNIFAC Activity Coefficient Calculator version 3.0¹³ with procedure 6A of 1986, with which the docosane was composed by 2 molecules of subgroup CH₃ and 20 molecules of CH₂ and heptane was composed by 2 and 5 molecules of subgroups CH₃ and CH₂, respectively. The values of parameters R and Q were extracted from the program and are shown in Table 1. More details are given by Fredenslund.¹⁴

Regular Solution Theory^{4,5,12} For nonpolar solvent and solute molecules using only pure component data the

Table 2. Solubility of Docosane (1) in Heptane (2)

<i>T</i> /K	x_1	<i>T</i> /K	x_1	<i>T</i> /K	x_1
277.25	0.0225	295.35	0.1556	304.75	0.3561
283.15	0.0440	297.35	0.1873	305.55	0.3922
286.25	0.0647	298.75	0.2166	307.65	0.4668
289.30	0.0844	301.45	0.2694		
290.95	0.1033	302.35	0.2932		

Table 3. Solubility of Docosane (1) in Heptane (2) from Ultrasound Measurements

x_1	<i>T</i> /K		
	expt 1	expt 2	expt 3
0.0225	277.25	277.30	277.20
0.1873	297.40	297.30	297.35
0.4668	307.60	307.70	307.65

activity coefficient can be predicted by the Scatchard–Hildebrand relation

$$RT \ln \gamma_1 = v_1 (\delta_1 - \delta_2)^2 \phi_2^2 \quad (5)$$

where v_1 is the molar volume of pure solute, δ_1 and δ_2 are the solubility parameters of the solvent and solute, respectively, and ϕ_2 is the volume fraction of the solvent, calculated by

$$\phi_2 = x_2 v_2 / (x_1 v_1 + x_2 v_2) \quad (6)$$

where x_i denotes the mole fraction. The solubility parameter δ_i defined by

$$\delta_i = (\Delta U_i^{\text{vap}}/v_i)^{1/2} \quad (7)$$

where ΔU_i^{vap} is the molar energy of vaporization for the pure component i and ΔH_i^{vap} is the molar enthalpy of vaporization of pure component i at temperature T . The value of ΔU_i^{vap} could be calculated from the molar enthalpy of vaporization or by the difference between the molar enthalpies of sublimation and fusion of the component i , both at the same arbitrary temperature T .

$$\Delta U_i^{\text{vap}} = \Delta H_i^{\text{vap}} - RT = \Delta H_i^{\text{sub}} - \Delta H_i^{\text{fus}} - RT \quad (8)$$

Those two methods were used to estimate the activity coefficient in eq 4 for a nonideal system.

Results

The solubility of docosane in heptane was measured in the temperature interval (277.25–307.65) K. The results are given in Table 2, where T represents the saturation temperature of the solution in which the docosane has a mole fraction x_1 .

It was found that the ultrasound did not influence docosane solubility in heptane solutions. The values for the system solubility under ultrasound conditions are shown in Table 3.

The measured solubility in the region of temperature and concentration studied is well represented by the equation proposed by Nývlt⁹

$$\log_{10} x_1 = A + \frac{B}{T} + C \log_{10} T \quad (9)$$

with $A = 19.0175$, $B = -3980.1740$, and $C = -2.5733$. This equation was used to estimate the amount of solids produced in the batch experiments because direct measurement was not practical. This equation can also be used

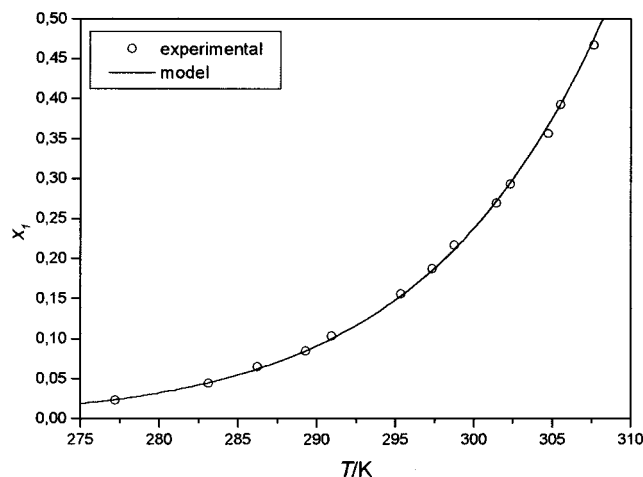


Figure 2. Solubility of docosane (1) in heptane (2).

Table 4. Some Activity Coefficients for the Docosane (1)–Heptane (2) System

T/K	γ_1 calculated by	
	UNIFAC method	regular solution theory
290.95	0.635	1.095
301.45	0.802	1.041
305.55	0.875	1.021

to evaluate the initial concentration x_1 for batch experiments starting from a solution saturated at a temperature T_{eq} and cooled to a temperature T_f .^{1,2} Figure 2 shows the experimental data and the curve fitted by the model of eq 9. The mean relative difference observed between the experimental data and the model was 0.52%.

Discussion

The experimental values of the system solubility were compared with two evaluations of solubility data by eq 2 and 4 for ideal solution and by eq 4 using the UNIFAC Method and Regular Solution Theory to estimate the activity coefficient. In both case, the thermodynamic and physical property data for docosane (1) and heptane (2) have been taken from the NIST Standard Reference Data Program,¹⁵ and they were near those from Kniaz's work³ ($MW_1 = 310.60 \text{ g}\cdot\text{mol}^{-1}$; $\rho_1 = 0.7644 \text{ g}\cdot\text{cm}^{-3}$; $MW_2 = 100.20 \text{ g}\cdot\text{mol}^{-1}$; $\rho_2 = 0.684 \text{ g}\cdot\text{cm}^{-3}$; $\Delta H_{f1} = 47801 \text{ J}\cdot\text{mol}^{-1}$; $T_m = 316.8 \text{ K}$; $\Delta H_{tr1} = 28605 \text{ J}\cdot\text{mol}^{-1}$; $T_{tr} = 315.5$; $\Delta H_1^{sub} = 172600 \text{ J}\cdot\text{mol}^{-1}$; $T_1^{sub} = 391 \text{ K}$; $\Delta H_2^{vap} = 31770 \text{ J}\cdot\text{mol}^{-1}$; $T_2^{vap} = 371.6 \text{ K}$).

The activity coefficients calculated by UNIFAC were smaller than 1 (ideality), but the ones calculated by Regular Solution Theory were approximately equal to unity. These values are shown in Table 4.

The evaluated solubility of the system by these methods is shown in Figures 3 and 4.

The group contribution methods are very approximate, which explains the low values for the activity coefficient calculated by the UNIFAC Method. They are based on the assumption that a functional group within a molecule acts independently on other groups and that its contribution to a physical property of any molecule is the same. The method gives better results with increasing difference between the main groups.⁴ In this system, the two components (heptane and docosane) belongs to the same group (group 1).

The mean relative difference between the experimental data and the model given by eq 2 (considering only the

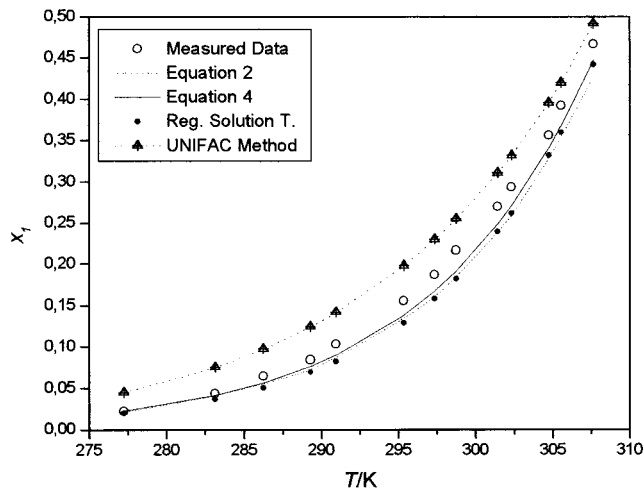


Figure 3. Evaluated solubility of docosane (1) in heptane (2).

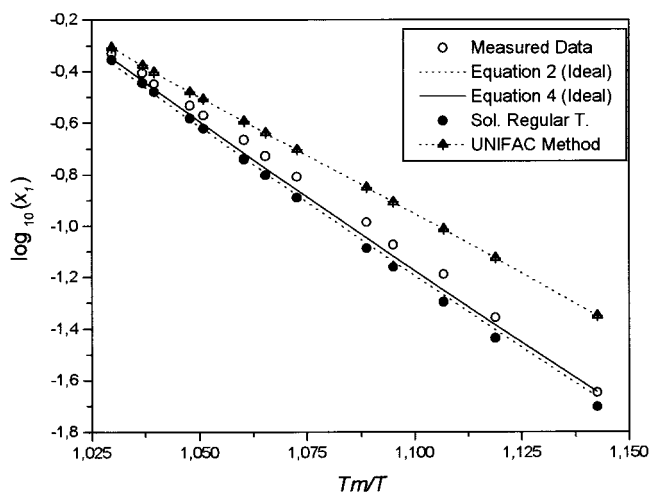


Figure 4. Evaluated solubility of the system in logarithm scale.

phase transition) was 2.79% and 1.86% between experimental data and eq 4 (considering the phase transition and the heat capacity on fusion) for an ideal solution ($\gamma = 1$). When the system was studied as a nonideal solution (assuming $\gamma \neq 1$), deviations between the experimental and calculated data were greater. For the Regular Solution Theory the results deviation was 2.69% and 3.80% for UNIFAC method. Therefore, the system can be interpreted as an ideal solution.

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