Solubilities of Tetracosane in Hydrocarbon Solvents

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The solubilities of tetracosane (n-$C_{24}H_{50}$) in heptane (n-C_7H_{16}), dodecane (n-$C_{12}H_{26}$), a mixture of isomers of decahydronaphthalene ($C_{10}H_{18}$), and *m*- and *p*-xylene (C_8H_{10}) have been determined over the temperature range 279.3–305.8 K. The results are well described by the equation $\ln x_2 = -(\Delta H^d/RT) + (\Delta S^d/R)$ for which the parameters ΔH^d and ΔS^d are given. The liquid-phase activity coefficients for the solid at 293.2 K have been derived from the measured solubilities and compared with values calculated from the Scatchard–Hildebrand equation and the UNIFAC group contribution method. Relatively good agreement is obtained using the Scatchard–Hildebrand equation, especially in the case of normal hydrocarbon solvents.

Determination of solubility data for a particular solute/solvent system is a prerequisite of crystal nucleation and growth studies. Such information is not generally available for higher normal alkanes dissolved in lower molecular weight hydrocarbons even though wax (higher *n*-alkanes) crystallization from fuel oils is a widespread problem on which extensive research has been undertaken (*1–4*).

Even assuming that all necessary thermodynamic properties are available, calculated ideal solubilities generally differ significantly from actual values (*5–10*) since 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. Measured solubilities can be used to determine activity coefficients of both the solute and solvent species if the enthalpies of fusion for the pure components are available. Although it is possible to estimate the activity coefficients using binary mixture experimental data or make predictions using empirical correlations, the mixture data are often unavailable and predictions from the available empirical correlations are frequently inaccurate.

In this paper we report results on solubilities of tetracosane (n-$C_{24}H_{50}$) in a number of hydrocarbon solvents: heptane (n-C_7H_{16}), dodecane (n-$C_{12}H_{26}$), a mixture of isomers of decahydronaphthalene ($C_{10}H_{18}$, decalin), and *m*- and *p*-xylene (C_8H_{10}, 1,3-dimethylbenzene and 1,4-dimethylbenzene, respectively). These were chosen as being representative of the types of molecules present in fuel oils. The activity coefficients determined from these solubility data are compared with those calculated from some of the accepted empirical expressions.

Experimental Procedure

Materials. The hydrocarbon materials used were supplied by either Fluka or Aldrich Chemical Co. Ltd. and had a guaranteed purity of >99 mass %. No other purifications were attempted since GC/MS analyses confirmed that impurity concentrations were at most 0.5 and generally less than 0.2 mass %.

The solvents were heptane of 99.8 mass % purity and boiling range 98–99 °C containing other heptane isomers as the main impurity, dodecane of 99.8 mass % purity and boiling point range 214–216 °C containing traces of branched alkanes, decahydronaphthalene of 99.8 mass % (60.9% *trans* and 38.9% *cis*) purity and boiling point range 189–191 °C containing methyl derivatives as the impurities, *m*-xylene with an assay of 99.5 mass % and boiling range 138–139 °C, and *p*-xylene of 99.8 mass % purity and melting and boiling point ranges 12–13 °C and 138 °C, respectively, the impurities made up mainly of the other two isomers.

The solute was tetracosane with an approximate assay of 99.9 mass % and melting point 50.4 °C containing docosane and pentacosane as the major impurities.

Method of Measurement. Solubilities were measured in a 20 cm^3 jacketed glass vessel thermostated by means of water circulating through the jacket. The thermostat maintained the required water temperature to within ±0.02 K. The vessel was tightly closed by means of a Teflon stopper through which was inserted a calibrated thermocouple connected to a Hewlett-Packard 3490A multimeter, giving an accuracy in the temperature measurement of ±0.01 K.

For each solubility measurement weighed amounts of solvent and solute were placed into the vessel and stirred magnetically at a constant rate. Initially the temperature was increased so as to ensure that all the solid material crystals dissolved. The saturation temperature was then determined by alternately cooling and heating the system over decreasing temperature intervals, so inducing nucleation and dissolution of crystals, respectively. The appearance and disappearance of the crystals were observed visually, and the equilibrium temperature was taken to be that at which the last crystal disappeared or no single crystal appeared after keeping the temperature constant for more than 12 h. It was estimated that the equilibrium temperature could be determined to within ±0.02 K.

For the sample of $C_{24}H_{50}$, the melting point and enthalpy of fusion at the melting point were determined by means of differential scanning calorimetry (DSC).

Estimation of Activity Coefficients

Methods Based on Regular Solution Theory (*11*). For nonpolar solvent and solute molecules using only pure component data the activity coefficient can be predicted by the Scatchard–Hildebrand relation:

$$RT \ln \gamma_2 = \upsilon_2(\delta_1 - \delta_2)^2 \phi_1^2 \tag{1}$$

where υ_2 is the molar volume of pure solute at temperature T, δ_1 and δ_2 are the solubility parameters of the solvent and solute, respectively, and ϕ_1 is the volume fraction of the solvent

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Table I. Solubilities of Tetracosane (n-$C_{24}H_{50}$) in Five Different Solvents

	concentration			concentration	
T/K	g/100 g of solvent	10^2x	T/K	g/100 g of solvent	10^2x
		Heptane (n-C_7H_{16})			
279.31	3.414	1.000	291.59	15.298	4.331
282.34	4.981	1.452	300.18	29.739	8.088
288.77	10.897	3.124	303.38	63.428	15.803
		Dodecane (n-$C_{12}H_{26}$)			
282.00	2.364	1.175	297.74	16.257	7.559
287.70	4.782	2.379	300.35	22.659	10.231
294.79	11.255	5.358	305.82	44.411	18.259
		Decalin (Decahydronaphthalene)			
280.73	4.131	1.658	292.42	17.113	6.530
283.84	5.772	2.302	295.70	24.074	8.948
287.84	10.003	3.923	299.79	37.492	13.273
291.10	14.381	5.545	303.21	55.607	18.500
		m-Xylene			
281.66	3.365	1.044	291.76	13.031	3.925
284.15	4.672	1.444	298.56	31.515	8.991
286.12	6.173	1.899	301.48	46.272	12.668
		p-Xylene			
286.73	7.398	2.267	297.33	29.138	8.370
289.81	10.873	3.296	300.49	43.820	12.078
294.75	17.883	5.309	303.27	60.918	16.035

given by

$$\phi_1 = x_1 v_1/(x_1 v_1 + x_2 v_2) \tag{2}$$

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

$$\delta_i = (\Delta U_i/v_i)^{1/2} \tag{3}$$

where ΔU_i is the energy of vaporization for pure component i. At temperatures well below the critical temperature

$$\Delta U_i = \Delta H_{vi} - RT \tag{4}$$

ΔH_{vi} being the molar enthalpy of vaporization of pure component i at temperature T. In subsequent calculations the molar volume was determined from

$$v_i = \mathrm{MW}/\rho_i^{20}$$

where ρ_i^{20} is the density of component i at 20 °C.

Group Contribution UNIFAC Method. This is based on the assumption that a physical property of a compound is the sum of contributions made by all the functional groups in the molecule. The molecular activity coefficient is separated into two parts, combinational and residual. The former is due to differences in the shape and size of the molecules in the mixture while the latter arises from interactions between structural groups. Both the size of the functional groups and the interaction areas are taken from pure component molecular structure data. Full details are given by Fredenslund et al. (*12*) while data used in these calculations were obtained from published sources (*13–15*).

Results

The solubilities of tetracosane in the five different solvents were determined over the temperature range 279.31–305.82 K. The results are given in Table I.

If it is assumed that a solute/solvent pair forms an ideal solution, the activity coefficient of the solute in the solvent equals unity and the solubility can be expressed by

$$\ln x_2 = -\frac{\Delta_s^l H}{RT}\left[1 - \frac{T}{T_m}\right] \tag{5}$$

where $\Delta_s^l H$ is the enthalpy of fusion of the solute at the melting point of the pure solid, T_m. The dashed line in Figure 1 represents the ideal solubility calculated using the literature values (*16*) for $C_{24}H_{50}$ of $\Delta_s^l H$ = 54.9 kJ/mol and T_m = 323.75 K. For comparison the experimentally determined solubilities of n-$C_{24}H_{50}$ in three of the solvents which are very different in structure (dodecane, m-xylene, and decahydronaphthalene) are also shown. The slopes of the straight lines calculated from the experimental data differ from the slope of this dashed line.

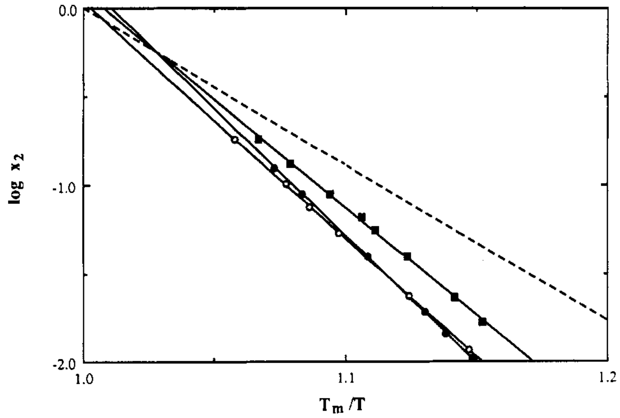

Figure 1. Measured solubilities of n-$C_{24}H_{50}$ in dodecane (○), decahydronaphthalene (■), and m-xylene (●). Ideal solubility curve calculated from eq 5 (- - -).

Table II. Parameters of the Solubility Curves

solute	solvent	ΔH^d/ (kJ mol^{-1})	ΔS^d/ (J mol^{-1} K^{-1})
n-$C_{24}H_{50}$	heptane	80.8 ± 0.0	250.9 ± 0.0
	dodecane	82.8 ± 0.0	256.5 ± 0.1
	decahydronaphthalene	75.6 ± 0.1	235.6 ± 0.2
	m-xylene	89.1 ± 0.0	287.3 ± 0.1
	p-xylene	86.7 ± 0.1	270.5 ± 0.4

For an ideal solution the enthalpy of fusion can be calculated from the slope of the straight line obtained by plotting ln x_2 against T^{-1} while the entropy of fusion, $\Delta_s^l S$, is obtained from the intercept since

$$\Delta_s^l S = \Delta_s^l H/T_m \tag{6}$$

so that from eq 5

$$\ln x_2 = -\frac{\Delta_s^l H}{RT} + \frac{\Delta_s^l S}{R} \tag{7}$$

The straight line parameters involved in dissolution of $C_{24}H_{50}$, ΔH^d and ΔS^d, in the five examined solvents are recorded in Table II.

Since the systems studied in this work show nonideal behavior, the activity coefficients differ from unity. At equilibrium between the solid solution (s) and the liquid solution (l) the isofugacity criterion applies:

$$f_2^s = \gamma_2 x_2 f_2^l$$

where a negligible solubility of the solvent in the solute is assumed and where these two fugacities are independent of the solvent and only dependent on the solid-phase properties. The following equation should then be considered (*11, 17*):

$$\ln x_2\gamma_2 = -\frac{\Delta_s^l H(T_t)}{RT}\left[1 - \frac{T}{T_t}\right] + \frac{\Delta C_p}{R}\left[\frac{T_t - T}{T}\right] - \frac{\Delta C_p}{R}\ln\frac{T_t}{T} \tag{8}$$

with γ_2 being the liquid-phase activity coefficient of the solute, $\Delta_s^l H(T_t)$ the enthalpy of fusion of the solute at the triple-point temperature T_t, and ΔC_p the change on fusion of the

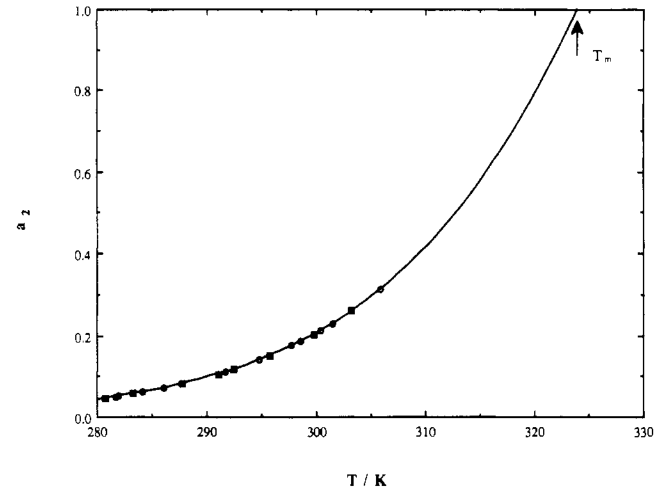

Figure 2. Activities of n-$C_{24}H_{50}$ in dodecane (○), decahydronaphthalene (■), and m-xylene (●) as a function of temperature. At the melting point, T_m, the activity $a_2 = 1$.

molar heat capacity of the pure solute. If the normal melting temperature, T_m, is substituted for T_t and the heat of fusion at the melting temperature, $\Delta_s^l H$, for $\Delta_s^l H(T_t)$, only a slight error is introduced (*11, 17, 18*). Furthermore, the terms which include ΔC_p can be neglected since their contribution to this exponential function is very small and can be assumed to be zero if the melting temperature of the solute is not more than about 100 K above the temperatures of the solutions, T (*11*).

Experimental DSC measurements gave the values $\Delta_s^l H$ = 54.3 kJ/mol and T_m = 323.5 K. These experimentally determined values were used to determine γ_2. Activities, $a_2 = x_2\gamma_2$, as a function of absolute temperature are shown in Figure 2. The continuous line is the best representation of the experimental data. At the melting point the activity would reach the value $a_2 = 1$.

Discussion

Although the solubilitites of tetracosane in the five different solvents all give linear plots when plotted as ln x_2 against T_m/T (for example, Figure 1), all these plots differ from the ideal solubility curve calculated using eq 5 with literature values of $\Delta_s^l H$ and T_m. This ideal solubility is therefore represented by

$$\ln x_2 = -6603.0(T/\mathrm{K})^{-1} + 20.395 \qquad (9)$$

All the observed solubilities are lower than predicted from this equation, and so the assumption of ideal solution is not appropriate. This may be attributed to the molar excess enthalpy and entropy resulting from the interaction forces when mixing molecules of different sizes and shapes (*15*), as well as to the variation of the enthalpy of fusion with temperature which should be taken into account.

Madsen and Boistelle (*8*) proposed that the enthalpy and entropy of fusion in eq 7 should be replaced by ΔH^d and ΔS^d, the parameters determined by a linear regression analysis in which the excess enthalpy was incorporated. These researchers have compared the values of ΔH^d with $\Delta_s^l H + \Delta H^{tr}$ (the enthalpy of phase transition) as a measure of the nonideality of the system.

For normal tetracosane ΔH^{tr} = 31.3 kJ/mol (*14*), so that $\Delta_s^l H + \Delta H^{tr}$ = 86.2 kJ/mol. Following the suggestion of Madsen and Boistelle (*8*) this value may be compared with the parameters listed in Table II. The lowest value for ΔH^d is obtained with decahydronaphthalene as solvent. p- and m-xylene, on the other hand, give higher values than $\Delta_s^l H + \Delta H^{tr}$. The normal alkane solvents n-heptane and n-dodecane, which belong to the same homologous series as the solute, give a somewhat lower value of ΔH^d compared to $\Delta_s^l H + \Delta H^{tr}$, but the value increases on increasing the chain length of the solvent molecule. Values of ΔS^d follow the same trend.

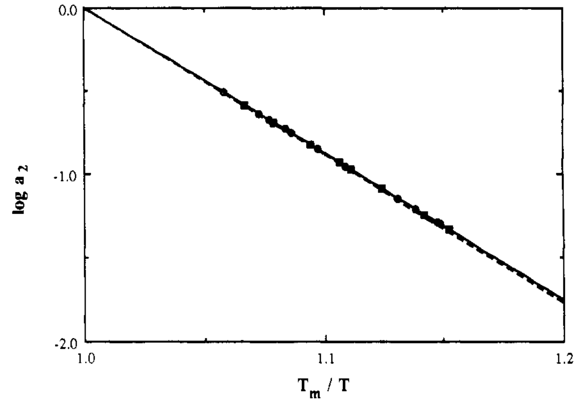

Figure 3. log a_2 as a function of T_m/T obtained for n-$C_{24}H_{50}$ in dodecane (○), decahydronaphthalene (■), and m-xylene (●) compared with the ideal solubility curve.

One might expect (*19*) decahydronaphthalene to have higher values of ΔH^d and ΔS^d than is found since its molecular structure differs significantly from that of tetracosane. However, the excess entropy of mixing for these two molecules and/or the molar excess enthalpy seem to be lower than for the other systems examined in this work. It could be that the solubility of n-$C_{24}H_{50}$ was not the same in each of the *cis* and *trans* isomers of which the solvent was composed. Although the two isomers are chemically similar, the intermolecular forces between solvent and solute molecules probably lead to a different endothermic heat of solution for each isomer. Besides, there are factors other than intermolecular forces which also play a role in the solubility of a solid and become important in such cases. A similar finding has been reported by Beiny and Mullin (*10*) who have found that the enthalpy and entropy of dissolution for each of the three higher n-alkanes ($C_{28}H_{58}$, $C_{32}H_{66}$, and $C_{36}H_{74}$) in a range of identical solvents did not follow the same rule. They also reported high values of ΔH^d and ΔS^d if the solvent was m-xylene.

In cases where a significant difference in size and nature of solvent and solute molecules exists (*11*), it would be expected that the activity coefficient would differ from unity, in nonpolar solutions, as is the present case, being in general greater than unity. Thus, the solubility calculated from eq 5 is lower than that corresponding to the ideal one.

Since there is no general method for predicting activity coefficients of solid solutes in liquid solvents, we have attempted to evaluate the saturation activity of n-$C_{24}H_{50}$ in the five solvents (Figure 2) from eq 8 using the experimentally determined values of solubility, enthalpy of fusion, and melting point temperature of the pure solid. A very small deviation from the ideal curve is still evident if log a_2 is plotted against T_m/T as can be seen from Figure 3. The reason for this difference most probably follows from the simplifications made in eq 8 and from introducing the experimental value for $\Delta_s^l H$ (54.3 kJ/mol) which slightly differs from the literature value (54.9 kJ/mol).

As an alternative to the obtained activity coefficients, two empirical correlations were used to predict the activity coefficients in the five examined systems. The results are summarized in Table III. The activity coefficients at 293 K evaluated from eqs 1 and 4 are compared with those calculated from the experimentally obtained solubilities.

The Scatchard–Hildebrand relation provides a relatively good approximation especially in the case of normal hydrocarbon solvents. As the difference in molecular size and

Table III. Activity Coefficients, γ_2, at 293.15 K Evaluated Using the Solubility Data (a) and the Scatchard-Hildebrand (b) and UNIFAC Method (c) Correlations

solute	solvent	γ_2 a	γ_2 b	γ_2 c
n-$C_{24}H_{50}$	heptane	2.394	3.177	0.456
	dodecane	2.759	1.979	0.812
	decahydronaphthalene	1.825	1.001	0.674
	m-xylene	2.668	1.008	0.752
	p-xylene	2.541	1.003	0.742

chemical nature of the components increases, the differences in γ_2 become larger. Somewhat better values for γ_2 could be obtained if the integral equation

$$RT \ln \gamma_2 = v_2[(\delta_1 - \delta_2)^2 + 2l_{12}\delta_1\delta_2]\phi_1^2 \qquad (10)$$

was used instead of its first approximation, eq 1, in which the binary parameter l_{12} is taken as zero. However, such an approximation is possible for the mixtures of hydrocarbons since l_{12} in nonpolar mixtures is small compared to unity. To evaluate l_{12}, at least one binary parameter is needed because no successful correlation of this parameter with pure component properties has been found (*20, 21*). An inaccurate estimate may lead to an incorrect activity coefficient, especially if the value of l_{12} is small and/or if there is a small difference between δ_1 and δ_2.

Much less accurate activity coefficients were calculated by means of the UNIFAC method, with all the values being less than unity. This could be expected since the group contribution methods are very approximate. 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 groups.

Since all the empirical correlations for activity coefficient prediction were established for a particular system, reasonably accurate predictions can only be made for systems similar to those for which the correlation was established; otherwise thermodynamic properties of a system are needed to evaluate the activity coefficients.

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