

Solubility of Long-Chain *n*-Alkanes in Petroleum Ether

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The solubilities of nonadecane (1–19 °C), tetracosane (5–24 °C), octacosane (6–28 °C), dotriacontane (9–31 °C), and hexatriacontane (12–34 °C) in petroleum ether have been determined. The results follow with high accuracy a relation of the form $\ln x_2(T) = \ln x_2(T_0) + (\Delta H_d/R)(1/T_0 - 1/T)$. Values of ΔH_d and of $x_2(T_0)$ for $T_0 = 25$ °C are given. ΔH_d is not very different from $\Delta H_{tr} + \Delta H_{fus}$.

In a number of studies of crystal growth of octacosane and hexatriacontane from solution (1, 3, 4, 8, 9, 13), we had to determine the solubilities of the long-chain *n*-alkanes in petroleum ether. Certain solubility data for related systems may be found in literature (5, 11, 12), but the required information was not available. As our results may be useful to other workers in the field of petroleum chemistry, we present them in this paper.

Experimental Section

The solvent was pure petroleum ether from Prolabo (trade mark of Rhone-Poulenc S.A.) with a stated boiling range of 35–60 °C. Its composition, determined by gas chromatography at the laboratory of the Société Française de Raffinage, was as follows: pentane, 35.86% w/w; methylbutane, 1.14; 2-methylpentane, 29.80; 3-methylpentane, 8.75; 2,2-dimethylbutane, 3.52; 2,3-dimethylbutane, 6.80; cyclopentane, 10.78; hexane, 2.39; total, 99.04% w/w.

A number of hydrocarbons of similar molecular weight made up the remaining 0.96%. The mean molecular weight is thus equal to 78.52.

The solutes were recrystallized Fluka products. They exhibited sharp transition and melting points in good agreement with literature data (7).

The remaining experimental details have been published elsewhere (9). In short, the saturation temperature of a solution of known concentration is determined by alternate raising and lowering of the temperature and observing the appearance and disappearance of crystals. This method yielded a precision of about 0.1 °C.

Results

Solubilities were determined for nonadecane, tetracosane, octacosane, dotriacontane, and hexatriacontane. The results for the five systems are given in Table I, where x_2 is the mole fraction of solute. When $\ln x_2$ is plotted as a function of $1/T$, a straight line is obtained. Hence, our data may be represented by the two-parameter equation

$$\ln x_2(T) = \ln x_2(T_0) + (\Delta H_d/R)(1/T_0 - 1/T) \quad (1)$$

where we shall refer to ΔH_d as the enthalpy of solution, though it is not, in general, identical with a calorimetrically determined value, because the solution is not ideal. With $T_0 = 25$ °C = 298.15 K, we find, by linear regression analysis (2), the values and standard deviations of $x_2(T_0)$ and ΔH_d given in Table II. The

Table I. Solubilities of the Five Alkanes in Petroleum Ether

T , °C	x_2	T , °C	x_2	T , °C	x_2
A. Nonadecane					
1.1	0.08946	10.5	0.2100	14.1	0.2805
3.1	0.1084	11.5	0.2262	14.3	0.2863
5.5	0.1331	12.9	0.2560	15.2	0.3094
8.0	0.1699	13.6	0.2753	19.0	0.4184
9.5	0.1896				
T , °C	$10^2 x_2$	T , °C	$10^2 x_2$	T , °C	$10^2 x_2$
B. Tetracosane					
5.1	0.8886	17.8	4.432	21.5	6.503
7.3	1.196	18.8	4.750	22.6	7.365
12.5	2.266	20.0	5.497	23.8	8.487
17.7	4.181				
C. Octacosane					
6.0	0.1425	10.8	0.2978	22.2	1.582
7.4	0.1730	12.6	0.4013	25.8	2.398
8.2	0.2018	13.3	0.4289	26.8	2.710
9.4	0.2454	17.2	0.7584	27.1	2.897
D. Dotriacontane					
9.4	0.04973	19.4	0.2361	25.5	0.5812
11.4	0.06984	19.4	0.2334	26.3	0.6513
12.5	0.08729	19.8	0.2482	26.9	0.7204
14.7	0.1087	20.7	0.2729	27.7	0.7898
15.2	0.1218	20.8	0.2865	28.2	0.8669
15.9	0.1338	22.1	0.3471	28.6	0.9565
17.0	0.1565	22.2	0.3615	29.2	1.047
17.9	0.1841	23.5	0.4335	29.3	1.033
18.6	0.2012	25.0	0.5413	30.2	1.230
T , °C	$10^3 x_2$	T , °C	$10^3 x_2$	T , °C	$10^3 x_2$
E. Hexatriacontane					
12.2	0.09446	19.7	0.4025	27.7	1.546
13.8	0.1360	20.6	0.4644	28.4	1.701
14.2	0.1549	20.7	0.4644	28.8	1.855
14.3	0.1228	22.5	0.6191	29.1	2.009
15.5	0.1858	22.8	0.6810	29.6	2.318
16.0	0.1977	23.5	0.7892	29.7	2.164
17.4	0.2477	24.5	0.9284	30.0	2.472
17.7	0.2544	25.3	1.083	30.9	2.626
18.7	0.3329	26.4	1.237	32.5	3.541
19.4	0.3612	26.8	1.392	33.1	3.553

sums of the enthalpies of phase transitions and of fusion, $\Delta H_{tr} + \Delta H_{fus}$, are shown for comparison (7).

It should be noticed that the solubility at 25 °C given for nonadecane does not represent a stable equilibrium, because the transition point at 22.8 °C results in a change of slope of the solubility curve.

Discussion

The solubility of any solid substance follows the relation (9)

$$\left(\frac{\partial \ln x_2}{\partial (1/T)}\right)_p = - \frac{\Delta H_{fus} + H_2^E}{R[1 + (\partial \ln \gamma_2 / \partial \ln x_2)_{T,p}]} \quad (2)$$

where H_2^E is the partial molar excess enthalpy of solute in solution. Except for the nonadecane system, our solutions are sufficiently dilute such that we may neglect the second term in

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Table II. Solubilities at 25 °C and Enthalpies of Solution

Substance	Solubility at 25 °C		ΔH_d , kJ/mol	ΔH_{tr} , kJ/mol	ΔH_{fus} , kJ/mol	$\Delta H_{tr} + \Delta H_{fus}$, kJ/mol	T_{tr} , °C	T_{fus} , °C
	$10^3 x_2$	g/100 g of PE						
C ₁₉ H ₄₀	681 ± 8	730 ± 9	57.5 ± 0.3	13.8	45.8	59.6	22.8	32.0
C ₂₄ H ₅₀	98 ± 2	47 ± 1	83.1 ± 0.8	31.3	54.9	86.2	48.1	50.9
C ₂₈ H ₅₈	22.1 ± 0.6	11.4 ± 0.3	99.3 ± 0.7	35.4	64.6	100.0	58.0	61.2
C ₃₂ H ₆₆	5.4 ± 0.2	3.1 ± 0.1	109.0 ± 0.8	?	?	115.8	63.5	70.2
C ₃₆ H ₇₄	0.99 ± 0.05	0.64 ± 0.03	128.5 ± 1.1	9.9	88.8	129.2	72.1	75.9
				30.5			73.8	

the denominator (law of ideality of dilute solutions). H_2^E is zero for an ideal solution, and if ΔH_{fus} is treated as a constant, eq 2 may be integrated to yield the well-known relation

$$\ln x_2 = (\Delta H_{fus}/R)(1/T_{fus} - 1/T) \quad (3)$$

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

$$\ln x_2 = \frac{\Delta H_{fus}}{R} \left(\frac{1}{T_{fus}} - \frac{1}{T} \right) + \frac{\Delta H_{fus} + \Delta H_{tr}}{R} \left(\frac{1}{T_{tr}} - \frac{1}{T} \right) \quad (4)$$

If we calculate the solubilities at 25 °C from eq 4, we find the following values for x_2 at 25 °C: C₁₉H₄₀, 0.655; C₂₄H₅₀, 0.069; C₂₈H₅₈, 0.0143; C₃₂H₆₆, 0.0021; C₃₆H₇₄, 0.000 55. From these values we see that the assumptions made in deriving eq 4 are not fulfilled for the actual systems. We arrive at the same conclusion from a comparison of the values of ΔH_d and $\Delta H_{fus} + \Delta H_{tr}$ in Table II. The causes for nonideality of the systems are (1) the nonvanishing of H_2^E and (2) the important excess entropy of mixing large and small molecules. The latter effect is accounted for by the Flory–Huggins theory (6, 10), whereas the

former seems more difficult to treat theoretically. In addition, the variation of ΔH_{fus} with temperature influences the solubility. We may conclude that the solubilities follow an equation of the form (3) or (4), but with the enthalpies and transition temperatures replaced by slightly different values.

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Gas Chromatographic Characterization of Phosphate Esters

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The gas chromatographic technique was employed in order to characterize four phosphate esters, which are at present used as plasticizers for plastic materials. The four phosphate esters were employed as stationary phases, while 22 organic compounds (hydrocarbons, alcohols, and acetates) were employed as GLC solutes. The investigation was carried out over a large range of temperatures. The four esters were classified according to Novak's polarity scale. Their insertion in the analogous classification for phthalate, adipate, and sebacate esters resulted in a 14-term polarity scale which suggests a new scientific criterion for the selection of the most suitable plasticizer to be used with polymeric systems.

At present, gas chromatography is considered one of the most suitable techniques for the determination of thermodynamic properties, such as activity coefficients, which provide useful indications among the components of liquid mixtures. On this basis, in the present study four phosphate esters were charac-

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terized by GLC. The present work is the continuation of the investigations started (1–3, 5, 6, 10) with a series of phthalate, adipate, and sebacate esters. These classes of compounds are widely employed as plasticizers for plastics, varnishes, etc. (13), to which they impart flexibility and shock resistance at reasonable prices.

Theory

The relationship which correlates the specific retention volume, V_g , with gas chromatographic quantities is the following (8)

$$V_g = \frac{F}{W_s} j \frac{P_o - P_{H_2O}^0}{760} \frac{273}{T_o} (t_R - t_a) \quad (1)$$

where j is the James–Martin factor (9) defined as

$$j = \frac{3(P_i/P_o)^2 - 1}{2(P_i/P_o) - 1} \quad (2)$$

Activity coefficients at infinite dilution, γ_i^∞ , are calculated by means of the following equation (7)

$$\ln \gamma_i^\infty = \ln \frac{273R}{V_{g,i} P_i^0 M_s} - \frac{B_{ii} P_i^0}{RT} \quad (3)$$