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Solubilities of Two n-Alkanes in Various Solvents

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Solubilities and phase equilibria of n-octadecane and n-dotriacontane have been determined in the following solvents: n-heptane, ethanol, ethanol/water mixtures, tributyrin, trioctanoin, and mixed triglycerides. In addition, temperatures and heats of fusion and transition of the two n-alkanes were measured by differential scanning calorimetry, in order to estimate the ideal solubility as a function of temperature.

Introduction

Linear polyethylene is composed of a distribution of n-alkanes of different molecular weight. The lower molecular weight oligomer fractions may have reasonably high solubility in various solvents. The study of the solubilities of low molecular weight alkanes in various solvents and in the polymers themselves will lead to their partition coefficients when a polymer is in contact with any of the solvents. Partition coefficients are useful in predicting the maximum or equilibrium levels of migration of these low molecular weight components from the polymer into contacting solvents when estimating migration from food packaging materials into food (*1*). The literature concerning the solubilities of these alkanes in the solvents of concern listed below is very limited (*2*). We report here observed solubilities and phase equilibria for two n-alkanes, n-octadecane and n-dotriacontane, in a variety of solvents including water, ethanol, ethanol/water mixtures, n-heptane, and triglycerides. Melting points and heats of fusion were determined calorimetrically in order to compare the observed and ideal solubilities.

Experimental Section

Techniques. In most cases, the solubilities were determined by visually observing the dissolution temperature of a mixture of solvent and solute of known composition. The mixture was encased with magnetic stirrer in a 5-mL vial and then submerged in a temperature-controlled bath. The temperature of the bath was lowered and raised at a very slow rate. The temperature at which dissolution was complete or precipitation began, as detected visually, was noted. The dissolution temperature and the precipitation temperature, in general, agreed well within 0.1 K.

For lower solubilities, where the visual method became impractical, ^{14}C-radiolabeled tracers were used. With a sensitive liquid scintillation counter operating at 20–30-cpm background, it was possible to detect the presence of 10^{-10} g of the labeled alkanes in aliquots taken from the solution. Labeled alkanes diluted by nonlabeled counterparts were used for higher-concentration experiments. It is particularly important to avoid the formation of a colloidal solution and the contamination of the aliquots by finely suspended particles when dealing with sparingly soluble species. In these cases, the lowest reproducible set of values from all the tests were considered to be valid solubilities.

The solubilities in mixed triglycerides were not determined as precisely as in other solvents, in view of the fact that the compositions of the food oil tested vary. The high viscosity of the solvents and solutions also prevented good separation in taking aliquots. The solubilities were estimated from a series of compositions left in a constant-temperature environment under occasional shaking. The 10 °C (283 K) experiments were performed at the average operational temperature in the liquid scintillation counter.

Table I. Solubility of n-Octadecane in Ethanol

t, °C	solubility, wt %	t, °C	solubility, wt %
10 (solid)	0.89	59.5	28.4
30.3	13.1	64.1	36.1
41.9	17.0	64.4	36.6
52.2	22.2		

The calorimetric measurements were performed with a Perkin-Elmer DSC-2 differential scanning calorimeter. (Certain commercial materials and equipment are identified in this paper to adequately specify the experimental procedure. This identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.) Samples weighing less than 2 mg were sealed in liquid-type aluminum sample containers. A scan speed of 5 K min^{-1} was used throughout. The temperature indicator was calibrated by measuring the melting points of high-purity o-terphenyl, calorimetry conference standard benzoic acid, and indium. The differential power signal or the energy was calibrated by measuring the heats of fusion of benzoic acid and indium. The heat of fusion of a small sample of o-terphenyl is difficult to determine because of supercooling. The melting points of benzoic acid and indium were reproducible within 0.1 and 0.3 K for different samples. The heats of fusion of benzoic acid were reproducible within ±1.5% and that of indium within ±2.5%. The mean calibration constant generated by benzoic acid was 3% higher than that by indium.

Materials. Commercially available n-alkanes and solvents were used directly without further purification. Our gas-chromatographic analysis indicated that the purity of n-heptane was 96.5%. The vendor's analysis indicated a purity of 97.1% with the impurities composed of various branched and cyclic isomers of heptane. The manufacturer quoted the purities of n-$C_{18}H_{38}$ and n-$C_{32}H_{66}$ as 97%. The purity of the commercially available 200-proof ethyl alcohol was believed to be 99.9+%. The water content of the ethanol used for the current solubility studies was determined by the same automatic Karl Fischer titration method as used for the characterization of NBS-SRM 1821, ethanol (forensic standard). The water content in ethanol samples taken from (a) a new 4-L jug, (b) a jug opened about 6 months ago but seldom accessed, and (c) a jug with only 1 L of ethanol remaining and being exposed quite frequently to the laboratory atmosphere during a period of 1 yr are 0.039, 0.082, and 0.090%, respectively. The water content in the standard reference material was 0.02%. The Karl Fischer instrument was calibrated via 1-butanol saturated with 0.196 weight fraction of water at 21 °C. Ethanol/water mixtures were prepared from the above-mentioned absolute alcohol and distilled water by weight.

The specific activities of the radioactive n-octadecane, n-$C_{18}H_{38}$-*1*-^{14}C, and n-dotriacontane, n-$C_{32}H_{66}$-*16,17*-$^{14}C_2$, are 0.086 and 0.046 Ci g^{-1} or 22 and 21 Ci mol^{-1}, respectively.

Results

Solubilities of n-octadecane in ethanol are listed in Table I and shown in Figure 1 for n-$C_{18}H_{38}$ in both liquid and crystalline

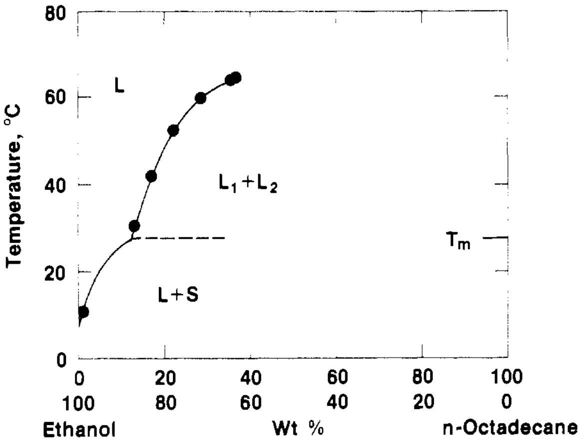

Figure 1. Phase diagram for *n*-octadecane in ethanol.

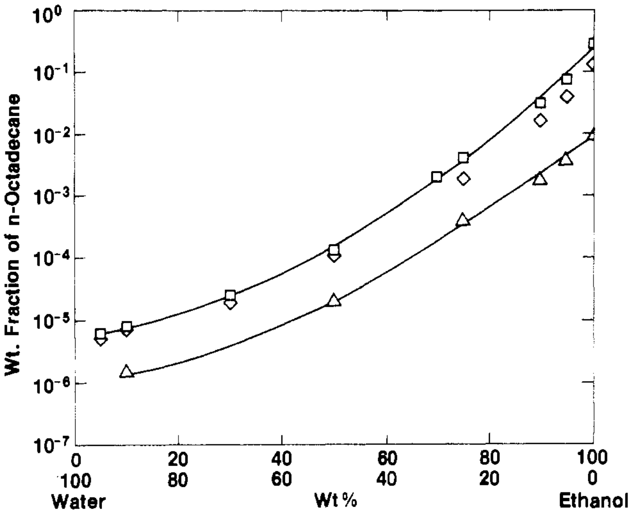

Figure 2. Solubility of *n*-octadecane in ethanol/water mixtures: (△) 10, (◇) 30, and (□) 60 °C.

Table II. Solubility of *n*-Octadecane in Ethanol/Water System

$[C_2H_5OH]$, wt %	$[n\text{-}C_{18}H_{38}]$, wt % 10 °C (solid)	 30 °C	 60 °C
0	1.2×10^{-5}	1.5×10^{-5}	1.7×10^{-5}
5		5×10^{-4}	6×10^{-4}
10	1.5×10^{-4}	7×10^{-4}	8×10^{-4}
30		1.9×10^{-3}	2.5×10^{-3}
50	0.0019	0.011	0.013
70			0.2
75	0.037	0.18	0.4
90	0.18	0.1	3.1
95	0.36	3.1	7.4
100	0.89	13	29

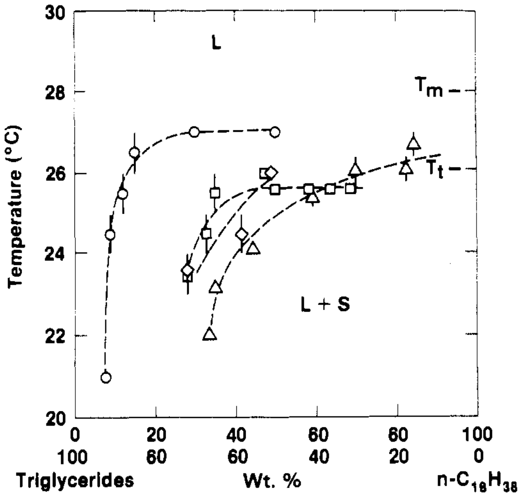

Figure 3. Phase diagram for *n*-octadecane in triglycerides: (○) tributyrin, (△) trioctanoin, (□) corn oil, (◇) mixed vegetable oil.

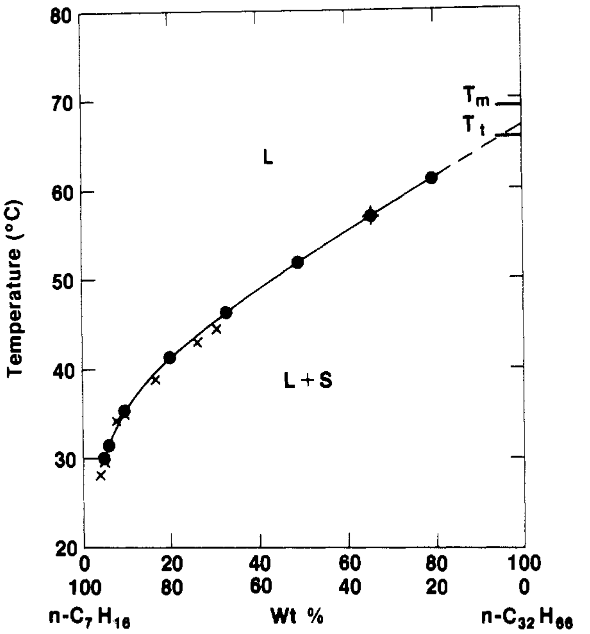

Figure 4. Phase diagram for *n*-doctriacontane in *n*-heptane: (●) this research, (+) graph (*2*), (×) table (*2*).

Table III. Solubility of *n*-Dotriacontane in Ethanol, 1-Octanol, and Tributyrin

t, °C	solubility, wt % ethanol	 1-octanol	 tributyrin
30	0.0081	0.27	0.030
60	0.71	17	2.0
65	2.9	67	40.0

Table IV. Solubility of *n*-Dotriacontane in *n*-Heptane

t, °C	solubility, wt %	*t*, °C	solubility, wt %
29.9	4.91	46.4	33.2
31.5	6.04	51.7	49.9
35.1	9.76	56.3	66.6
41.3	20.1	60.9	80.2

states. The liquid states are denoted in the figures by L, L_1, and L_2. The solid state is denoted by S.

The solubilities of *n*-octadecane in the ethanol/water system are listed in Table II and shown in Figure 2 for three temperatures. The solubilities vary over a range of seven decades. Most of the data were generated by means of various dilutions of ^{14}C-labeled *n*-octadecane.

Above the melting point of 28.2 °C, liquid *n*-octadecane appears to be miscible with *n*-heptane, pure or mixed triglycerides, and 1-octanol.

The solubilities of solid *n*-octadecane in pure and mixed triglycerides are shown graphically in Figure 3. The solubility of $n\text{-}C_{18}H_{38}$ is greater in the higher members of triglycerides. The solubilities in both corn oil and a mixed vegetable cooking oil are slightly less than that in trioctanoin but much higher than that in tributyrin. *n*-Octadecane appears to be miscible with triglycerides at about 1 K below its melting point. No attempt was made to analyze the compositions of the food oils or to determine the water contents in these triglycerides, which may have a significant impact on the solubilities of the alkanes.

The solubilities of $n\text{-}C_{32}H_{66}$ in ethanol, 1-octanol, and tributyrin are listed in Table III. The solubilities of $n\text{-}C_{32}H_{66}$ in $n\text{-}C_7H_{16}$

Table V. DSC Measurements on *n*-Octadecane and *n*-Dotriacontane

	n-$C_{18}H_{38}$	*n*-$C_{32}H_{66}$
T_t, K	299.1	338.9
ΔH_t, kJ mol^{-1}		42.7
T_m, K	301.1	342.1
ΔH_m, kJ mol^{-1}	59.4	76.0

are listed in Table IV and shown in Figure 4 together with that reported by Hildebrand and Wachter (*2*). Liquidus *n*-$C_{32}H_{66}$ has limited solubility in ethanol but is miscible with tributyrin and 1-octanol.

The amount of volatile solvent evaporated into the vapor space in the enclosed vial will increase the solute concentration. This effect is more pronounced at higher temperatures where the vapor pressure of the pure solvent is high. However, the effect is reduced by the high concentration of the solute or the low concentration of the solvent. Furthermore, the high ratio of solute over that of solvent at high temperature yields a smaller percentage correction to the solute than that of the solvent. The corrections to the vaporization are estimated iteratively from the equilibrium vapor pressure of the solvent, the original composition, and the vapor space. The maximum correction applied to the original composition to yield the values listed in Tables I and IV is less than 0.3 wt. %.

The mole fraction, N_2, and the weight fraction, X_2, of the solute may be converted from one to the other as follows:

$$N_2 = 1/[1 + (1/X_2 - 1)M_2/M_1] \quad (1)$$

$$X_2 = 1/[1 + (1/N_2 - 1)M_1/M_2] \quad (2)$$

where M_1 and M_2 are the molecular weights of the solvent and the solute, respectively. As noted in most textbooks of chemical thermodynamics and in ref *2*, for an ideal solution and considering a constant heat of fusion, ΔH_m, the solubility changes with temperature as

$$\ln N_2 = (\Delta H_m/R)(1/T_m - 1/T) \quad (3)$$

where R is the gas constant. From our solubility data and data from ref *2* for *n*-$C_{32}H_{66}$ in *n*-C_7H_{16}, a reasonable fit to eq 3 may be obtained by assigning a T_m of 340-340.65 K and a ΔH_m of 101 kJ mol^{-1}, as shown by the line in Figure 4. However, long-chain *n*-alkanes exist in a rotator phase just below their melting points.

Our differential scanning calorimeter measurements, Table V, on *n*-dotriacontane indicated a melting point of 342.1 K and a transition at 338.9 K, with heats of fusion and transition of 76.0 and 42.7 kJ mol^{-1}, respectively. The heat of transition was reproducible within 1% and that of fusion within 2% after the first scan. The melting points were reproducible within a span of 0.3 K and that of the transition within a span of 0.4 K. During the first scan the transition appeared to be broader and took place at 0.2-0.5 K higher, involving only half of the energy as required for subsequent scans. However, the melting point and the total energy for the transition and fusion remained the same regardless of the sample histories.

Table VI. Solubility of *n*-Octadecane in *n*-Heptane

t, °C	solubility, wt %	*t*, °C	solubility, wt %
0.0	21.3	8.4	38.4
8.0	37.0	9.0	39.5

Since all of the solubility measurements on *n*-$C_{32}H_{66}$ were performed below the transition, the hypothetical melting point of the low-temperature form at 340.65 K as estimated from solubility measurements is within the narrow span of the existence of a rotator phase from 338.9 to 342.1 K. This appeared to be a reasonable estimate of the intersection of the two free energy curves extending from the liquid phase and from the low-temperature phase, in the absence of the high-temperature rotator phase. The estimated heat of fusion of 101 kJ mol^{-1} for the low-temperature form is in reasonable agreement with the sum of the heats of transition and fusion, 121 kJ mol^{-1}, as measured calorimetrically. When the calorimetrically measured total energy was used as ΔH_m in eq 3, the estimated solubilities are lower than those measured at lower temperatures. This discrepancy is due largely to the effect of the differences in the heat capacities of the liquid and solid phases and hence a temperature dependency of the heat of fusion.

The melting point and the heat of fusion of *n*-octadecane were determined by DSC as 301.1 K and 59.4 kJ mol^{-1}, with similar uncertainties as that noted for *n*-dotriacontane. A transition, barely resolvable as a shoulder on the fusion peak, was suspected to occur at 299.1 K. According to eq 3, the ideal solubility of *n*-$C_{18}H_{38}$ at 0 and 8 °C (273.15 and 281.15 K) should be 19.5 and 36.5 wt %, respectively. The solubility of *n*-$C_{18}H_{38}$ in *n*-C_7H_{16} at 0 and 8 °C was determined as 21.3% and 37.0% by weight, Table VI. Thus, the solubility of *n*-$C_{18}H_{38}$ in *n*-C_7H_{16} may also be described reasonably well by eq 3. Above the melting point, *n*-octadecane is miscible in *n*-heptane. It appears that the miscibility of *n*-$C_{18}H_{38}$ and the triglycerides also occurs just below its melting point, at a temperature near or above the suspected transition temperature, Figure 3. Therefore, the observed solubility is slightly higher than that calculated with the melting point of the rotator phase. If the transition point is considered as the melting point of the low-temperature phase, the calculated solubilities are 22.7 and 41.4 wt % at 0 and 8 °C, respectively. Similar to the case of *n*-$C_{32}H_{66}$ in *n*-C_7H_{16}, the hypothetical melting point of the low-temperature phase is within the range of the rotator phase, 299.1-301.1 K.

Registry No. Octadecane, 593-45-3; dotriacontane, 544-85-4; heptane, 142-82-5; ethanol, 64-17-5; tributyrin, 60-01-5; trioctanoin, 538-23-8.

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(2) Hildebrand, J. H.; Wachter, A. *J. Phys. Chem.* **1949**, *53*, 886-90.

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