J. Chem. Eng. Data 1994, 39, 793−795

Solubility of Long-Chain *n*-Alkanes in Heptane between 280 and 350 K

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Solubilities of tetracosane, dotriacontane, hexatriacontane, and mixtures of hexatriacontane + dotriacontane in heptane were measured at temperatures ranging from 280 to 350 K at atmospheric pressure. Several equations were evaluated for their ability to predict the solubility in these systems. Comparisons between measurement and prediction are shown.

Introduction

Accumulation of waxy deposits is a commonly occurring problem during transportation of oil in pipelines. Removal of these undesirable wax deposits by methods such as the addition of chemical inhibitors, and heat tracing of flow lines, requires a knowledge of the solubility of long-chain alkanes in liquids such as heptane. A number of studies of the solubilities of alkanes in hexane and other solvents have been reported in the literature (*1*−*11*). In this work we report solubilities in the model systems hexatriacontane + heptane, dotriacontane + heptane, tetracosane + heptane, and hexatriacontane + dotriacontane + heptane in the temperature range from 280 to 350 K at atmospheric pressure.

Experimental Section

Solubilities were determined by visual observation of the dissolution temperature of a mixture of known composition. The solubility apparatus consisted of a jacketed glass vessel maintained at a constant temperature by water circulated from a water bath (GCA/Precision Scientific Circulating System 254). The jacket temperature could be maintained within ±0.01 K in the temperature range 258−433 K. Two sizes of jacketed vessels were used, with internal volumes of approximately 125 and 55 mL. The inner chambers of the vessels were baffled in order to facilitate mixing. Continuous stirring was achieved with a magnetic stir bar. One-holed stoppers were used to seal the inner chambers of the vessels from the atmosphere and prevent the evaporation of heptane. A mercury-in-glass thermometer, with a calibration traceable to NIST, was inserted through the hole in the stopper for the measurement of the temperature of the contents of the vessel. The thermometer had a measurement range from 272 to 374 K and an uncertainty of ±0.1 K.

Mixtures were prepared by mass using a Mettler H542 balance. The balance had a range of measurement up to 160 g, with an uncertainty of ±0.000 01 g. Masses above 160 g were measured using a Fisher XT top loading balance, with an uncertainty of ±0.001 g. The estimated error in the mole fractions was less than 0.001.

Liquid heptane and solid tetracosane, dotriacontane, and hexatriacontane were purchased from the Aldrich Chemical Co. The stated purities of the substances were 99, 99, 97, and 98 mol%, respectively. All of the materials were used without additional purification.

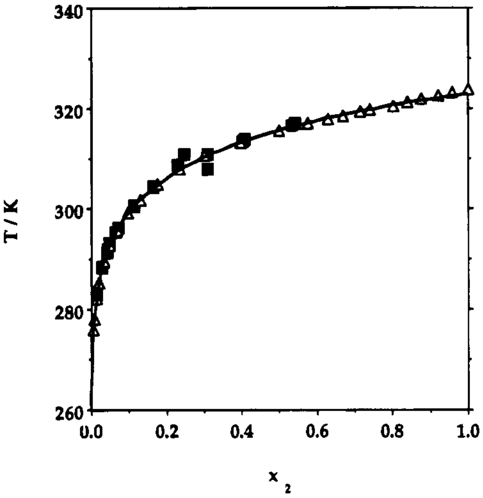

Figure 1. Solid−liquid equilibria in the system tetracosane + heptane. The experimental data of this work are represented by squares, whereas the data of Domasnska and Rolinska (*6*) are represented by triangles. The solid line was calculated using the equation of Haulait-Pirson et al. (*7*).

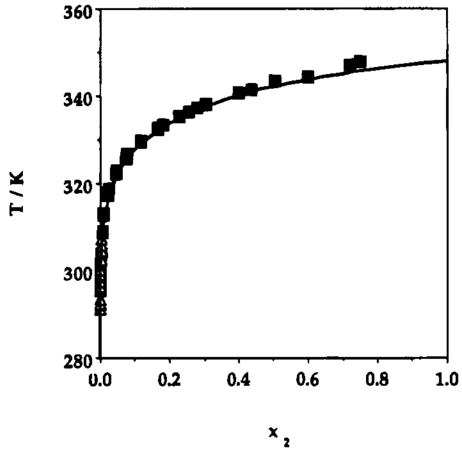

Figure 2. Solid−liquid equilibria in the system hexatriacontane + heptane. The experimental data of this work are represented by squares, whereas the data of Madsen and Boistelle (*3*) are represented by triangles. The solid line was calculated using the equation of Haulait-Pirson et al. (*7*).

The solubility of a solid *n*-paraffin in heptane was measured as follows. Predetermined amounts of heptane and the solid solute were weighed and deposited into the jacketed vessel. The contents of the vessel were heated very slowly at rates less than 2 Kelvin/ h, with continuous stirring. When the last observed portion of solute dissolved, the temperature was recorded as the liquidus temperature at the calculated composition of the binary

0021-9568/94/1739-0793$04.50/0

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

T_d/K	x_2	T_d/K	x_2
283.3	0.0147	300.7	0.1132
283.3	0.0148	304.4	0.1649
283.1	0.0149	304.3	0.1651
282.9	0.0150	308.7	0.2286
288.4	0.0285	310.9	0.2468
288.2	0.0286	310.8	0.3075
291.3	0.0425	308.0	0.3076
291.8	0.0426	313.4	0.4026
293.1	0.0491	313.9	0.4087
295.4	0.0651	316.6	0.5315
296.1	0.0696	317.1	0.5414
300.5	0.1127		

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

T_d/K	x_2	T_d/K	x_2
320.2	0.0971	327.0	0.1995
320.6	0.1001	326.8	0.1999

Table 3. Solubility of Hexatriacontane (2) in Heptane (1)

T_d/K	x_2	T_d/K	x_2
297.3	0.0005	326.0	0.0779
296.7	0.0005	326.8	0.0781
300.7	0.0011	329.4	0.1162
301.6	0.0013	329.4	0.1163
304.0	0.0021	329.8	0.1164
308.8	0.0051	332.7	0.1649
308.9	0.0052	332.5	0.1651
313.0	0.0105	333.4	0.1811
312.8	0.0105	335.4	0.2286
313.1	0.0105	336.3	0.2558
317.3	0.0214	337.4	0.2797
317.9	0.0216	338.0	0.3052
318.8	0.0257	340.8	0.4000
322.3	0.0469	341.4	0.4373
323.0	0.0471	343.4	0.5042
325.6	0.0728	344.4	0.5997

Table 4. Solubility of Hexatriacontane (3) + Dotriacontane (2) in Heptane

T_d/K	x_3	x_2	T_d/K	x_3	x_2
326.3	0.0412	0.0959	343.0	0.4743	0.0508
326.9	0.0485	0.0924	345.2	0.5639	0.0423
329.2	0.0731	0.0927	345.6	0.6498	0.0340
329.9	0.0926	0.0881	330.4	0.0407	0.1920
330.4	0.0958	0.0901	332.4	0.0818	0.1838
333.0	0.1400	0.0857	334.0	0.1230	0.1748
335.2	0.1856	0.0812	335.9	0.1837	0.1624
336.8	0.2314	0.0766	338.2	0.2490	0.1494
337.9	0.2788	0.0700	338.6	0.2554	0.1481
339.8	0.3271	0.0654	342.0	0.3960	0.1202
341.0	0.3761	0.0606	344.4	0.5459	0.0906
342.4	0.4245	0.0556	347.6	0.7192	0.0563
350.0	0.8772	0.0253			

solution. If the dimensions of the vessel allowed, a new predetermined mass of solute was added to the vessel contents, and the equilibrium temperature at this new composition was measured. The procedure for the measurement of ternary system solubility was very similar to that for binary systems. Predetermined amounts of heptane and dotriacontane, in a ratio of 1 mol of dotriacontane to 9 mol of heptane, were weighed, deposited into the vessel, and sealed. The vessel contents were heated, at the previously mentioned rate, until all of the solute was observed to dissolve into solution. The binary dissolution temperature of dotriacontane in heptane was recorded in the first two trial runs. Next, a measured mass of hexatriacontane was added to the vessel contents. The vessel was heated at the same heating rate, until crystals of this second solute were observed to dissolve into solution. The dissolution temperature of the hexatriacontane was recorded. This procedure was repeated for an initial dotriacontane + heptane solution of molar ratio about 1 to 4.

Results and Discussion

Measured solubilities of tetracosane, dotriacontane, and hexatriacontane in heptane at temperatures ranging from 280 to 350 K are presented in Tables 1−3. The results for the tetracosane + heptane system are shown in Figure 1 together with the measurements of Domanska and Rolinska (*6*), while the results for the hexatriacontane + heptane system are shown in Figure 2 together with the measurements of Madsen and Boistelle (*3*). In both cases, our data show good agreement with the literature values. Solubility data for the ternary system hexatriacontane + dotriacontane + heptane measured in this work are presented in Table 4.

The solubility x_2 of a solute 2 in a solvent 1 at temperature T was also calculated using the standard thermodynamic relationship for equilibrium between a pure solid solute and a liquid solution containing the solid (*6*):

$$\ln x_2 = (\Delta_{\mathrm{fus}}H/R)\{(1/T_{\mathrm{m}}) - (1/T)\} + (\Delta_{\mathrm{tr}}H/R)\{(1/T_{\mathrm{tr}}) - (1/T)\} - \ln \gamma_2 \quad (1)$$

In the above equation, T_m is the melting temperature of the solid solute and T_{tr} is the temperature of any solid−solid transition that the solute undergoes. The equation thus takes into consideration the existence of solid−solid phase transitions in the *n*-alkanes, and requires a knowledge of the activity coefficient γ_2 in the calculations. Contributions that arise from the heat capacity differences between the solid and liquid phases are assumed to be negligible in comparison with terms which arise from the enthalpy of fusion $\Delta_{fus}H$ and the enthalpy of transition $\Delta_{tr}H$.

Several simple predictive models for the calculation of γ_2 were examined in this work, including the ideal solution model

$$\ln \gamma_2 = 0 \quad (2)$$

the regular solution theory

$$RT \ln \gamma_2 = v_2 \phi_1^{\,2}[\delta_1 - \delta_2]^2 \quad (3)$$

the Flory−Huggins theory

$$\ln \gamma_2 = \ln(\phi_2/x_2) + 1 - (\phi_2/x_2) \quad (4)$$

and the Haulait-Pirson et al. (*7*) model

$$\ln \gamma_2 = (0.5)[\ln(\phi_2/x_2) + 1 - (\phi_2/x_2)] - (\phi_1^{\,2} v_2/RT)(\delta_1 - \delta_2)^2 \quad (5)$$

Table 5. Properties of the Alkane Components

n	T_m/K	$\Delta_{fus}H$/(kJ mol^{-1})	T_t/K	$\Delta_{tr}H$/(kJ mol^{-1})	$\Delta_{vap}H$ (kJ mol^{-1})	v/(cm^3 mol^{-1})
7	182.55 (*13*)	14.02 (*13*)			36.51 (*11*)	147.46 (*12*)
24	323.75 (*14*)	54.84 (*14*)	321.25 (*14*)	31.27 (*14*)	105.87 (*11*)	424.60 (*12*)
32	342.10 (*4*)	75.92 (*4*)	338.90 (*4*)	42.66 (*4*)	138.96 (*11*)	555.00 (*12*)
36	349.05 (*13*)	88.74 (*14*)	345.25 (*14*)	40.42 (*14*)	155.50 (*11*)	620.20 (*12*)

In the above equations, ϕ represents the volume fraction ($\phi_i = x_i v_i / \sum x_j v_j$) and δ is the solubility parameter ($\delta = [(\Delta_{\text{vap}}H - RT)/v]^{1/2}$). The properties of melting, vaporization, solid–solid phase transition, and the molar liquid volume required in the calculations were obtained from the literature and are given in Table 5 together with their sources.

The predictions from the ideal solubility model and regular solution theory underestimated the solubility in these alkane mixtures, whereas those of the Flory–Huggins theory overestimated the solubility. The Haulait-Pirson equation gave the best agreement between prediction and measurement. The predicted equilibrium curves using this equation are shown as solid lines in Figures 1 and 2.

Solubility data for the ternary system hexatriacontane + dotriacontane + heptane were also calculated using the above equations. In this case, the values calculated by the Flory–Huggins model significantly overestimated the ternary system solubility, whereas the Haulait-Pirson equation also overestimated the solubility, but to a lesser extent than the Flory–Huggins equation. Both the ideal solubility predictions and regular solution theory predictions were in good agreement with the experimental data.

Nomenclature

R	gas constant
T	temperature
T_{d}	dissolution temperature
T_{m}	melting temperature
T_{tr}	solid–solid phase transition temperature
v, v_i	liquid molar volume
x_i	mole fraction of component i
$\Delta_{\text{fus}}H$	molar enthalpy of fusion
$\Delta_{\text{tr}}H$	molar enthalpy of solid–solid phase transition
$\Delta_{\text{vap}}H$	molar enthalpy of vaporization
δ_i	solubility parameter of component i
ϕ_i	volume fraction of component i

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Received for review February 24, 1994. Accepted May 30, 1994.[⊗] We would like to thank the Exxon Foundation for financial support of this work.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1994.