J. Chem. Eng. Data **1991**, *36*, 471–472

Solubility of *n*-Docosane in *n*-Hexane and Cyclohexane

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The solubility of docosane (*n*-alkane C_{22}) in cyclohexane and *n*-hexane has been measured over a wide range of temperature. The eutectic point has been determined for the system *n*-docosane–cyclohexane. In both solvents a transition point crystal–rotator of solute has been observed. Three methods of solubility prediction have been applied in calculations: the Flory–Huggins theory, the Kikic–Alessi improved Flory expression, and the Hualait-Pirson formula for combinatorial entropy.

Introduction

The most common analytical, and possibly industrial, application of the solid–liquid phase equilibria consists of the separation, purification, and concentration of substances by crystallization. Crystallization is carried out by passing one or more liquid phases into a crystallizer held at a temperature between the freezing and melting point of the feed. When the phase equilibrium is reached, a solid phase and a liquid phase are formed which are withdrawn. It is desirable to know if the resultant material will be liquid, solid, or a mixture of both phases; in the latter case, the composition of each phase needs to be determined.

If the mathematical representations of solid–liquid equilibria are available, it is possible to set forth computational procedures to perform the necessary process design calculations.

Experimental Section

Docosane was purchased from FLUKA-AG (Buchs SG, CH); cyclohexane, from International Enzymes Ltd. (GB); and hexane, from REACHIM (SU). Hexane was purified by fractional distillation (refractive index: experimental value, n^{20} = 1.37475; literature value (*1*), n^{20} = 1.37486). Docosane (purum grade, melting point 317.05 K) and cyclohexane (refractive index: value from gas chromatography label, n^{20} = 1.42621, literature value (*1*), n^{20} = 1.42623) has been used without purification.

Solubilities were determined by a dynamic (synthetic) method. Mixtures of solute and solvent, prepared by weighing pure components, were heated very slowly (at least 2 K h^{-1} near the equilibrium temperature) with continuous stirring in a Pyrex-glass cell which was placed in a thermostat. The crystal disappearance temperatures detected visually were measured with a calibrated Anschutz (TGL 11996, H. Schlegel, Ilmenau, GDR) thermometer of a range from −50 to +50 °C, subdivided in 0.1 K, totally immersed in the thermostatic liquid.

Measurements were carried out for a wide range of solute mole fractions from 0 to 1 in cyclohexane and from 0.1 to 1 in hexane. The accuracy of the temperature measurements was ±0.05 K. The reproducibility of measurements was 0.1 K, which corresponded to a root error in composition $\sigma(x_1)$ = 0.0005. The measurements of solubility revealed the existence of the crystal–rotator phase transition in *n*-docosane. The temperature of the transition point determined through these investigations was 316.15 K. This experimental result is in agreement with the literature value (*2*). For the system *n*-docosane + cyclohexane, the eutectic point has been determined: T_e = 275.10 K, x_{1e} = 0.0195 (detected graphically).

Table I. Solubility Data of *n*-Docosane

x_1	T/K	x_1	T/K	x_1	T/K
		n-Docosane (1) + Cyclohexane (2)			
0.0000	279.65	0.1765	296.55	0.7116	313.65
0.0100	277.65	0.2113	298.70	0.7191	313.85
0.0133	276.75	0.2495	300.65	0.7540	314.15
0.0151	276.40	0.2872	302.55	0.7789	314.55
0.0207	275.60	0.3394	304.50	0.8077	314.85
0.0283	278.35	0.3572	305.25	0.8426	315.25
0.0346	280.00	0.3945	306.70	0.8619	315.40
0.0484	283.10	0.4114	307.00	0.8827	315.65
0.0589	285.00	0.4452	308.25	0.9156	316.10
0.0697	286.45	0.4993	309.40	0.9159	316.15
0.0795	287.80	0.5352	310.35	0.9258	316.30
0.0906	289.25	0.5749	311.05	0.9468	316.65
0.1093	291.35	0.6191	312.25	1.0000	317.05
0.1465	294.95	0.6749	313.25		
		n-Docosane (1) + *n*-Hexane (2)			
0.0889	291.25	0.5112	310.90	0.8007	314.95
0.1103	293.30	0.5371	311.40	0.8572	315.50
0.1312	295.30	0.5725	312.00	0.8679	315.65
0.1612	297.25	0.6214	312.70	0.9028	315.85
0.2024	300.15	0.6530	313.10	0.9263	316.05
0.2443	302.25	0.6706	313.45	0.9323	316.25
0.3043	304.90	0.7200	314.15	0.9562	316.55
0.3545	306.85	0.7534	314.40	0.9861	316.90
0.4406	309.30	0.7651	314.55	1.0000	317.05

Solid–liquid equilibrium data are listed in Table I.

Prediction and Discussion

The solubility of a solid in a liquid can be used to evaluate the activity coefficient of the solute component in the solution by eq 1. This equation is valid if no phase transition takes

$$\ln x_1 = -\frac{\Delta H_{m1}}{RT_m}\left[\frac{T_m}{T} - 1\right] + \frac{\Delta C_{pm1}}{R}\left[\ln\left(\frac{T}{T_{m1}}\right) + \frac{T_{m1}}{T} - 1\right] - \ln \gamma_1 \quad (1)$$

place in the solid phase between the system temperature T and the solute melting temperature T_{m1}.

When a phase transition takes place between T and T_{m1}, eq 1 must be modified to include the effect of the transition point. For the first-order phase transition eq 1 has a form

$$\ln x_1 = -\frac{\Delta H_{m1}}{RT_m}\left[\frac{T_m}{T} - 1\right] + \frac{\Delta C_{pm1}}{R}\left[\ln\left(\frac{T}{T_{m1}}\right) + \frac{T_{m1}}{T} - 1\right] - \frac{\Delta H_{tr1}}{RT_{tr1}}\left[\frac{T_{tr1}}{T} - 1\right] - \ln \gamma_1 \quad (2)$$

Experimental x_1 vs T data therefore permit evaluation of the activity coefficients of the solute γ_1 by using eq 1, or 2, provided the necessary physical properties of the solid are available.

The thermodynamic data for *n*-docosane have been taken from the classical work of Schaerer et al. (*2*): ΔH melting = 48.99 kJ mol^{-1}; ΔH phase transition = 28.22 kJ mol^{-1}.

Prediction of thermodynamic data is a markedly more difficult task than correlation. From the small number of parameters and data of pure substances–components of solution, thermo-

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0021-9568/91/1736-0471$02.50/0

Table II. Results of the Solubility Prediction

	σ,[a] %			
system	ideal	Flory–Huggins	modified Flory–Huggins	Haulait-Pirson
n-docosane + n-hexane	6.99	18.99	11.49	55.61
n-docosane + cyclohexane	10.22	17.4	4.93	65.85

[a] Deviation: $\sigma = (1/np)\sum_i|(x_{calc} - x_{expt})/x_{expt}| \times 100$.

dynamic features of their mixtures must be determined. A properly established model should take into account all thermodynamic phenomena of the considered system.

In the present work solutions formed by a long-chain solute and short-chain or globular solvent are considered. Such large differences in size affect the enthalpy and entropy of mixing; however, due to the enthalpy/entropy compensation effect (*3*), the free energy of mixing and the activity coefficient remain constant or only slightly changed. Therefore it might be interesting to compare the ideal solubility with the solubility predicted by using methods incoporating solute–solvent size differences.

The activity coefficient of the substance in the solution, where solvent and solute molecules differ appreciably in size according to the Flory–Huggins theory (*4*), is given by eq 3, where V_1, V_2

$$\ln \gamma_1 = \ln\left(\frac{\phi_1}{x_1}\right) + \phi_2\left[1 - \frac{V_1}{V_2}\right] \quad (3)$$

are the molar volumes of components 1, 2 (often replaced by the size factors r_1, r_2 taken from work of Bondi (5)), x_1 is the molar fraction (solubility) of component 1, ϕ_1, ϕ_2 are the volume (or size factor) fractions of both components.

It is commonly known that the Flory–Huggins theory overestimates the combinatorial entropy. In a quest to find a more adequate expression useful in the fluid-phase equilibria calculations, Alessi and Kikic (*6*) proposed some simple modifications in the Flory–Huggins formula. They applied size factor r_i raised to $^2/_3$. The Kikic–Alessi modification is used in the new UNIFAC model.

Recently Huyskens and Haulait-Pirson (*7*) have proposed a new expression for the combinatorial entropy of mixing. Haulait-Pirson applied this term in SLE prediction of n-alkanes (*8*):

$$\ln \gamma_1 = 0.5\phi_2\left[1 - \frac{V_1}{V_2}\right] + \ln \phi_1 - 0.5 \ln\left[\phi_1 + \phi_2\frac{V_1}{V_2}\right] - \ln x_1 \quad (4)$$

In order to obtain the calculated equilibrium mole fraction, the nonlinear equation for every experimental point i must be solved:

$$\ln a_i^{expt} = \ln a_i^{calc} \quad (5)$$

where $\ln a^{expt}$ is given by eq 1 or 2 and $\ln a^{calc}$ by eq 3 or 4. The results of solubility prediction, presented in the form of a mean deviation between the calculated and experimental mole fractions, are listed in Table II. Parts a and b of Figure 1 present differences between the ideal and predicted solubilities vs the experimental data. System n-docosane + n-hexane is almost ideal; therefore the classical Schroeder equation for the ideal solubility predicts the experimental data with the smallest error in composition (6.99%). The best results for the system n-docosane + cyclohexane have been achieved with the modified Flory–Huggins formula (6.5%). In both cases, the "classical" Flory–Huggins equation reveals significant deviations, as was anticipated. The Haulait-Pirson expression gives highly unsatisfactory results.

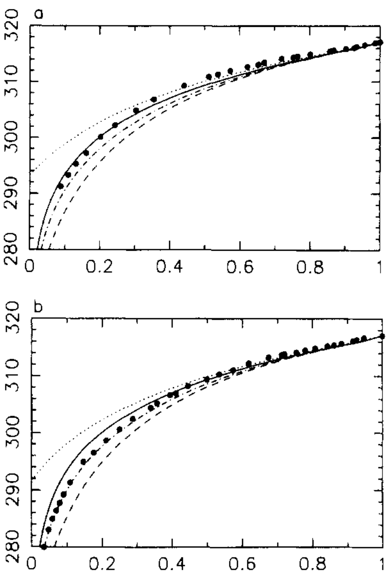

Figure 1. (a) Solubility prediction vs experimental data (filled circles) for the solubility of n-docosane in n-hexane: (—) ideal solubility; (- -) Flory–Huggins results; (– • –) modified Flory–Huggins results; (···) Haulait-Pirson results. (b) Solubility prediction vs experimental data (filled circles) for the solubility of n-docosane in cyclohexane: (—) ideal solubility; (- -) Flory–Huggins results; (– • –) modified Flory–Huggins results; (···) Haulait-Pirson results.

Acknowledgment

I thank Dr U. Domańska for her encouragement and fruitful discussions.

Glossary

ΔC_{pm}	difference of molar specific heat between those of liquid and solid at the fusion temperature, J mol^{-1} K^{-1}
ΔH_m	molar enthalpy change of fusion, J mol^{-1}
ΔH_{tr}	molar enthalpy change on transition, J mol^{-1}
r	group surface area of the molecule
R	gas constant
T	system temperature, K
T_m	melting temperature, K
T_{tr}	phase-transition temperature, K
T_e	eutectic point temperature, K
V	molar volume
x	mole fraction

Greek Letters

γ	activity coefficient
ϕ	volume fraction

Subscripts

1	solute
2	solvent

Registry No. $H_3C(CH_2)_{20}CH_3$, 629-97-0; $H_3C(CH_2)_4CH_3$, 110-54-3; cyclohexane, 110-82-7.

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Received for review March 14, 1990. Revised October 26, 1990. Accepted June 10, 1991.