

SOLUBILITIES OF SOLID n-ALKANES IN SUPERCRITICAL ETHANE

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ABSTRACT

The solubilities of solid n-triacontane ($n\text{-C}_{30}\text{H}_{62}$) and n-Dotriacontane ($n\text{-C}_{32}\text{H}_{66}$) in supercritical ethane at temperatures between 308K and 319K and pressures upto 20 MPa are reported in this work. The results have been correlated using an equation of state, using sublimation pressures which are extrapolated from data available for the lower even-numbered members of the alkane series.

INTRODUCTION

Then n-alkanes are an interesting series because they display great regularity in their behavior. Many of their fluid phase properties, for example, can be correlated with the number of carbon atoms in the molecules. In order to develop general relations for supercritical extraction, therefore we have studied the solubilities of solid n-alkanes in supercritical ethane. The solubilities of n-triacontane ($n\text{-C}_{30}\text{H}_{62}$) and n-dotriacontane ($n\text{-C}_{32}\text{H}_{66}$) in ethane are reported in this paper. Results for n-tetracosane ($n\text{-C}_{24}\text{H}_{50}$), n-hexacosane ($n\text{-C}_{26}\text{H}_{54}$) and n-octacosane ($n\text{-C}_{28}\text{H}_{58}$) will also be presented at the symposium. One reason for studying only the even-numbered members of the n-alkane series is that they exhibit different packing properties than the odd-numbered members of the series [1,2,3]. Thus their solid phase properties such as heats of sublimation and vapor pressures follow different trends from those of the odd-numbered members. This is shown in Fig. 1 for the heats of sublimation. Any generalizations for supercritical extraction of solids must therefore take account of this difference in behavior.

EXPERIMENTAL

The apparatus used in this study was a single-pass flow system shown

schematically in Fig. 2. The apparatus is similar in principle to those used by Kurnik et al [4] and others [5,6,7]. Solvent gas is first liquefied and then compressed past its critical pressure by means of a Milton Roy minipump A. Its temperature is increased to supercritical conditions in the heat exchange coil B immersed in a constant-temperature water bath C. The bath temperature was maintained constant to $\pm 0.1\text{K}$ and the temperature monitored by means of a copper-constantan thermocouple D calibrated against an NBS-certified platinum resistance thermometer. The pressure of the system was measured by a Heise gauge E calibrated against a dead-weight gauge. The pressure was maintained constant by a back pressure regulator F. The supercritical solvent was then brought into contact with the solute in a modified Jerguson equilibrium cell G. The equilibrium temperature was measured by a second copper-constantan thermocouple K calibrated against an NBS-certified platinum resistance thermometer. This thermocouple was inserted inside the cell by means of a fitting. For better solid contact, layers of glass beads were packed with the solute in the equilibrium cell. The loaded supercritical fluid was then depressurized at the micrometering valve H and the deposited solute was collected in a separation vessel J. The micrometering valve was heated to compensate for the Joule-Thompson effect upon depressurization and all the lines outside the constant temperature bath were heat traced. In spite of these precautions, however, some of the long-chain n-alkanes still precipitated inside the micrometering valve. This deposited solid was flushed out with liquid hexane at the end of each run. The solute collected was weighted to ± 0.10 mg using a Mettler electronic balance. Solvent volume was recorded using a wet test meter L. We estimate the precision of our temperature, pressure and volume measurements to be 0.5 K, 0.5 mmHg and $\pm 1/2\%$ respectively; the accuracies were typically twice the magnitude of the precision.

RESULTS

For comparison purposes, the solubilities of 2,3-dimethylnaphthalene in CO_2 along three isotherms were first measured and the results compared with those of Kurnik et al [4]. These results are presented in table 1 for the 308.15K isotherm. In no case did our solubilities differ from those of Kurnik et al by more than 3.6% for any of the isotherms.

Our results for the $C_2H_6 + n C_{30}H_{62}$ and $C_2H_6 + n C_{32}H_{66}$ systems are shown in Tables 2 and 3. Since the sublimation pressures of the higher n-alkanes were not available in the literature, we have treated these as adjustable parameters in our equation of state correlations of the solubility data. The sublimation pressures were not freely adjustable, however, but were bounded by the values obtained by extrapolating propane and n-octadecane sublimation pressures 25%. Our results are shown in Fig 3 and 4. Additional results will be discussed at the symposium. The equation of state used was that of Patel and Teja [8].

REFERENCES

1. Morawetz, E., "Ethalpies Of Vaporization from C_{12} to C_{20} ", J. Chem. Thermo. 4, 139 (1972).
2. Bondi, A., "Heat of Sublimation of Molecular Crystals A Catalog of Molecular Structure Increments", J. Chem. Eng. Data 8, 371 (1963).
3. Broadhurst, M. G., J. Res. Nat. Bur. Stand. A 66, 241, (1962).
4. Kurnik, R. T., Holla, S. J. and Reid, R. C., "Solubility of Solids in Supercritical Carbon Dioxide and Ethylene", J. Chem. Data, 26, 47 (1981).
5. Adachi, Y., Benjamin, C. and Lu, Y., "Supercritical Fluid Extraction with Carbon Dioxide and Ethylene", Fluid Phase Equil., 14, 147 (1983).
6. Mchugh, M. A. and Paulaitis, M. E., "Solid Solubilities of Naphthalene and Biphenyl in Supercritical Carbon dioxide", J. Chem. Eng. Data, 25, 326 (1980).
7. Johnston, K. P. and Eckert, C. A., "Analytical Carnahan-Starling-van der Waals Model for Solubility of Hydrocarbon Solids in Supercritical Fluids", AIChE J., 27, 773-779 (1981).
8. Patel, N. C. and Teja, A. S., "A New Cubic Equation of State for Fluids and Fluid Mixtures", Chem. Eng. Sci., 37, 463 (1982).

TABLE I

Comparison of CO₂ + 2,3 Dimethylnaphthalene
Data at 308.15K

System Pressure MPa	Y _{2,3-DMN} × 10 ³	
	This Work	Kurnik et al
9.87	2.28	2.2
14.25	4.36	4.41
19.60	5.45	5.42
24.12	5.76	5.82
27.92	6.45	6.43

TABLE II

Results for Ethane-n-Triacontane (C₃₀H₆₂)

System Pressure MPa	Y _{C₃₀H₆₂} × 10 ³	
	308.15K	313.15K
6.57	0.549	0.486
10.10	1.24	1.95
13.64	1.71	3.50
16.67	2.24	
20.20	3.20	

TABLE III

Results for Ethane-n-Dotriacontane (C₃₂H₆₆)

System Pressure MPa	Y _{C₃₂H₆₆} × 10 ³		
	308.15K	313.15K	319.15K
6.57	0.216	0.177	0.149
10.10	0.713	0.953	1.28
13.64	0.958	1.44	2.14
16.67	1.26	1.73	
20.20	1.81	2.18	

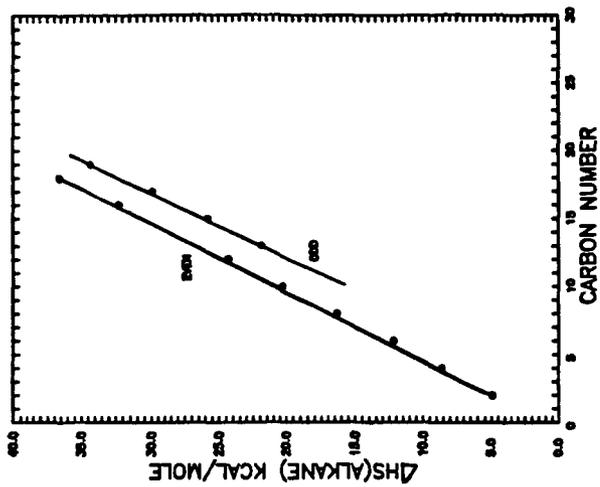


Figure 1. Heat of Sublimation vs. Carbon Number

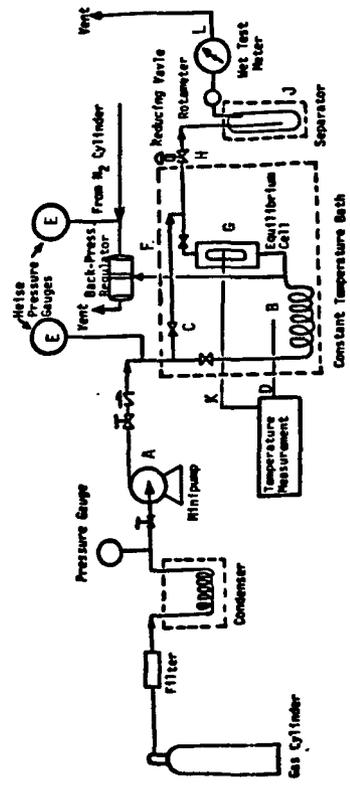


Figure 2. Supercritical Flow Apparatus

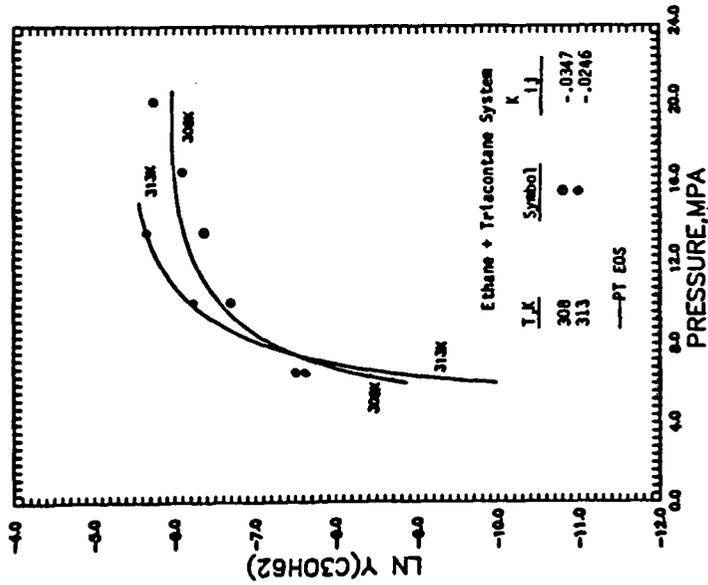


Figure 3. Solubility of Triscontane in Supercritical Ethane

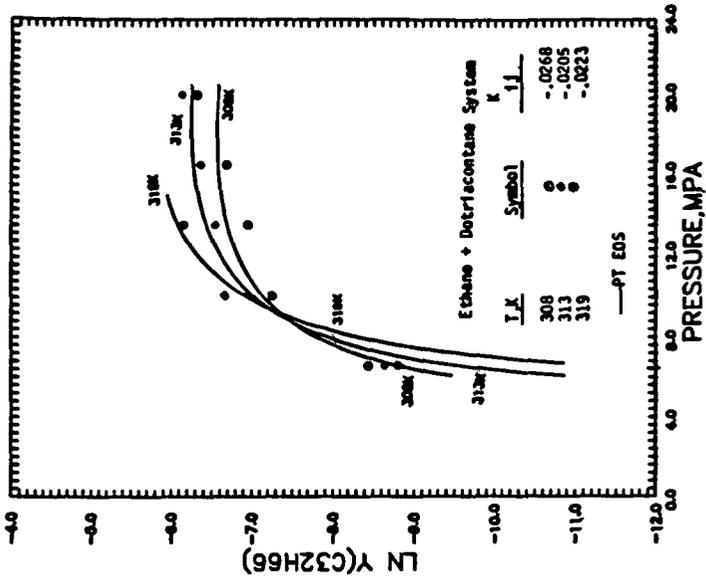


Figure 4. Solubility of Dotriscontane in Supercritical Ethane