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SEPARATION OF ALKANES AND AROMATICS WITH SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

The separation of alkanes and aromatics with supercritical carbon dioxide has been studied by measuring vapour-liquid equilibria and selectivities in the model systems 2-methylnaphthalene/hexadecane/ carbon dioxide and 2-methylnaphthalene/dodecane/carbon dioxide. The results have been modelled with the Peng-Robinson equation of state. In both model systems supercritical carbon dioxide appeared selective for the component with the highest vapour pressure, 2-methylnaphthalene respectively dodecane. Consequently alkanes and aromatics will be separated by supercritical carbon dioxide on basis of their difference in vapour pressure instead of their difference in chemical structure.

INTRODUCTION

Supercritical extraction is gaining increased attention as an alternative for conventional separation techniques such as liquid extraction and distillation. One reason is the easy solvent/ extract and solvent/raffinate separation. Another is that the properties of temperature sensitive products are preserved since supercritical extractors are operated at moderate temperatures (25-100 °C). Most of the applications of supercritical extraction concern the extraction of natural raw materials with carbon dioxide in the food, flavour and pharmaceutical industry [1-4]. Although on the other hand the separation of alcohol-water mixtures and the extraction of organic pollutants from waste water have been studied intensively [1-4], little research effort has been directed to the separation of liquid hydrocarbon mixtures with supercritical solvents.

This article presents the results of a study of the separation of alkanes and aromatics with supercritical carbon dioxide. In the petrochemical industry the separation of alkanes and aromatics with polar solvents is one of the most important applications of liquid extraction for separating hydrocarbon mixtures [5]. Previous studies of the use of supercritical carbon dioxide made by Kulkarni [6] and Dhalewadikar [7] have shown that the alkanes are selectively extracted when the alkanes and aromatics that are to be separated posses equal molecular weights. In this study the effect of pressure, temperature, composition and volatility of the components on the selectivity and capacity of the supercritical solvent (carbon dioxide) have been measured. The results were modelled with the Peng-Robinson equation of state.

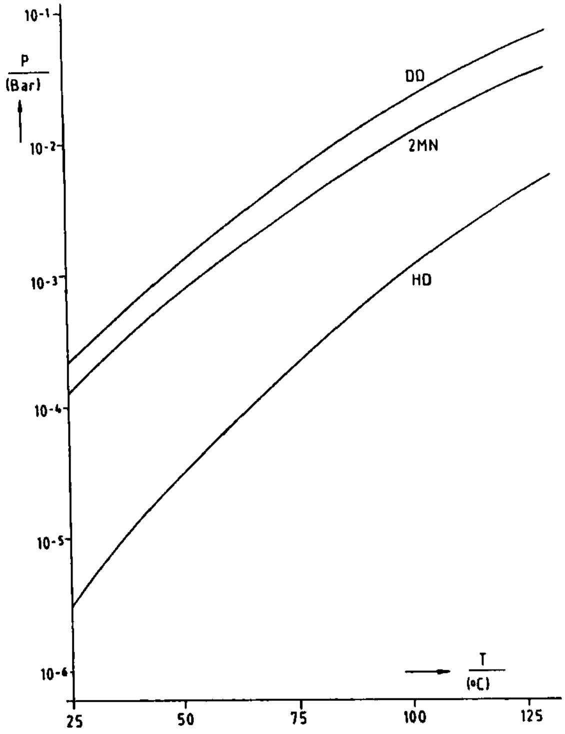

Fig.1. Vapour pressure of dodecane (DD), 2-methylnaphthalene (2MN) and hexadecane (HD) as a function of temperature [13].

MODEL COMPONENTS

In our study 2-methylnaphthalene (aromatic) and hexadecane (alkane) were used as model components. The phase behaviour of the ternary system can be obtained by considering the three binary mixtures that comprise the ternary model system. Parts of the Px-isotherms of the binary systems hexadecane/CO_2 [8,9] and 2-methylnaphthalene/CO_2 [6,10] can be taken from the literature. Figure 1 shows that 2-methylnaphthalene has a higher vapour pressure than hexadecane. The influence of the vapour pressure of the components on the selectivity and capacity of supercritical carbon dioxide was demonstrated by replacing hexadecane by dodecane. The Px-isotherms of the binary system dodecane/CO_2 [11,12] are available in the literature. Since there is no information available about the binary systems 2-methylnaphthalene/hexadecane and 2-methylnaphthalene/dodecane, ternary equilibrium data were used to model the binary systems.

CALCULATION PHASE EQUILIBRIA

Vapour-liquid equilibria at high pressures are conveniently calculated by using an equation of state applicable to both phases [1,13]. The condition for equilibrium between the vapour and the liquid phase is given by:

$$f_i^L(P,T,x_i) = f_i^V(P,T,y_i) \qquad (1)$$

$$x_i\,\phi_i^L\,P = y_i\,\phi_i^V\,P \qquad (2)$$

The fugacity coefficients ϕ_i^L and ϕ_i^V are calculated from an equation of state [13]. We have chosen to use the Peng-Robinson equation [14]:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \qquad (3)$$

The pure component parameters a(T) and b were calculated from the critical properties of the components [14] and mixed according to the following mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad i,j = 1,2,\ \ldots,n \qquad (4)$$

$$a_{ij} = (1-\delta_{ij})(a_{ii}a_{jj})^{1/2} \qquad (5)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \qquad i,j = 1,2,\ \ldots,n \qquad (6)$$

$$b_{ij} = (1-\eta_{ij})(b_{ii} + b_{jj})/2 \qquad (7)$$

The values for the binary interaction parameters δ_{ij} and η_{ij}, obtained from binary and ternary PTx-data, are listed in table 1.

Table 1 : Calculated binary interaction parameters.

Components	δ_{ij}	η_{ij}	ref.
CO_2 + dodecane	0.09	0.06	11,12
CO_2 + hexadecane	0.08	0.02	8,9
CO_2 + 2-methylnaphthalene	0.07	-0.05	6,10
dodecane + 2-methylnaphthalene	0.02	0.03	
hexadecane + 2-methylnaphthalene	0.00	0.02	

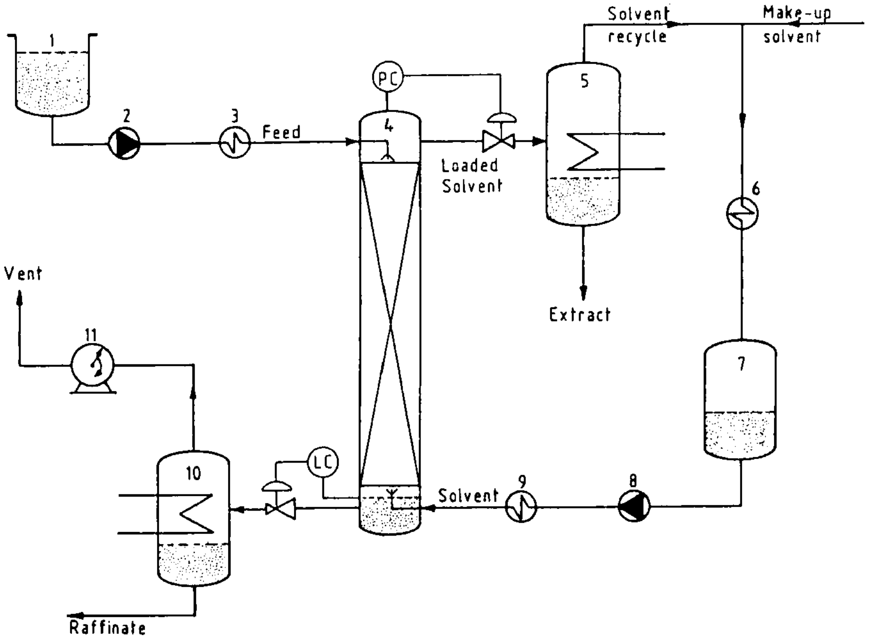

Fig.2. Flowsheet of the supercritical extraction equipment.
(1)Storage vessel feed, (2)Pump, (3)Heat exchanger, (4)Column, (5)Separator, (6)Condensor, (7)Storage Vessel CO_2, (8)Pump, (9)Heat exchanger, (10)Separator, (11)Wet gas meter

EXPERIMENTAL

A simplified flowsheet of the experimental equipment is shown in figure 2. The feed was fed to the top of the extraction column (4). This column, with an internal diameter of of 35 mm and a length of 1 m, was equipped with 60 cm Sulzer BX laboratory packing. The remaining raffinate, containing a considerable amount of carbon dioxide, was drawn off from the bottom of the column. Hereafter the pressure was reduced to 1 bar to separate the carbon dioxide from the alkane/ aromatic mixture (10). A wet gas meter (11) was used to measure the carbon dioxide flow and the raffinate was periodically drawn off.

The supercritical carbon dioxide entered the bottom of the column and left the top of the column containing the dissolved extract. The pressure was reduced below the critical pressure of carbon dioxide (50-60 bar) to condense the extract in the separator (5). This extract was periodically drawn off. By measuring the carbon dioxide flow to the extraction column with a Micro Motion mass flowmeter, the amount of carbon dioxide in which the extract was dissolved was calculated from a carbon dioxide mass balance over the column. The gaseous carbon dioxide was condensed before increasing the pressure again to the extraction pressure (8).

A small solvent to feed ratio was used to measure the selectivity and capacity of the supercritical carbon dioxide. It appeared that under these circumstances only 5 to 15 percent of the feed was extracted and that the extract stream leaving the column was in equilibrium with the liquid flowing down in the top of the column consisting of the feed saturated with carbon dioxide. This amount of dissolved carbon dioxide was assumed to be equal to the amount dissolved in the raffinate, that appeared to have nearly the same composition as the feed. A refractometer was used to measure the composition of the solvent free feed, raffinate and extract. The relative variance in the measured vapour and liquid phase compositions appeared to be approximately 5 percent.

The dodecane, 99% purity, was obtained from Jansen Chimica. The hexadecane, 99% purity, and the 2-methylnaphthalene, 96% purity, were bought from MERCK-Schuchardt. Hoek-Loos supplied the 99.99% pure carbon dioxide. All these materials were used without further purification.

RESULTS

Phase Behaviour of the Model System

Figures 3 and 4 show the measured and calculated vapour-liquid equilibria of the model system 2-methylnaphthalene/hexadecane/ carbon dioxide at a temperature of 80 °C. At a pressure of 150 bar only small amounts of 2-methylnaphthalene and hexadecane dissolve in the vapour phase while a considerable amount of carbon dioxide dissolves in the liquid phase. When the pressure is increased from 150 to 200 bar it can be seen from figure 4 that the solubilities of 2-methylnaphthalene and hexadecane in the vapour phase are increased markedly. Also more carbon dioxide is dissolved in the liquid phase at this pressure. The strong curvature of the liquid branch at this pressure illustrates that carbon dioxide is less soluble in 2-methylnaphthalene than hexadecane.

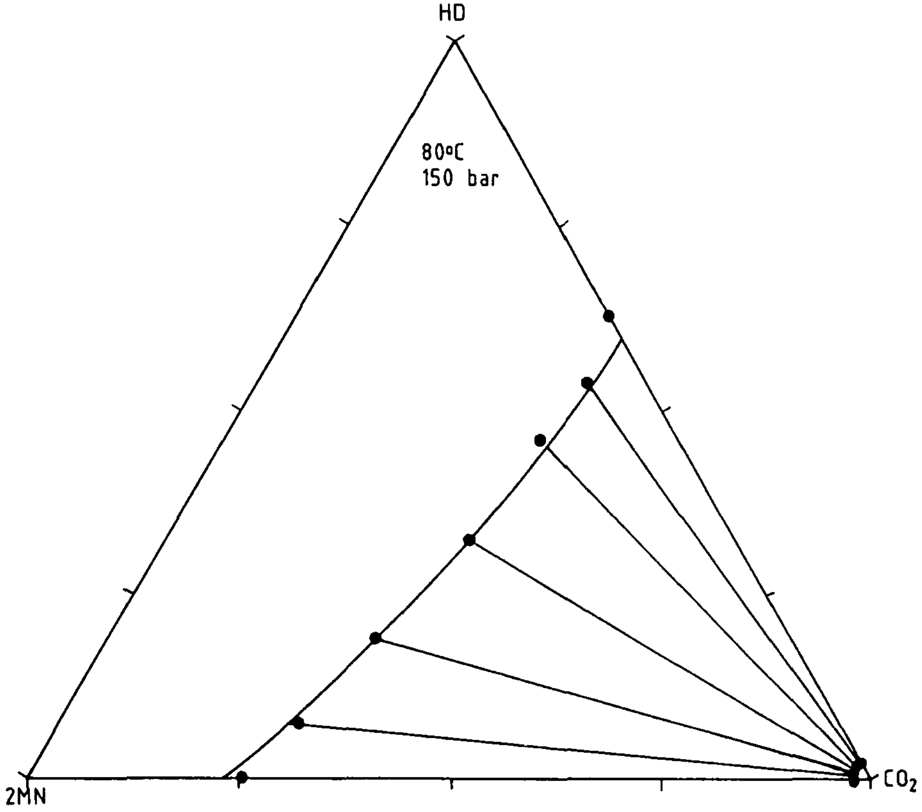

Fig.3. Measured (●) and calculated (-) vapour-liquid equilibria (%wt) of the model system 2-methylnaphthalene/hexadecane/ carbon dioxide at 80 °C and 150 bar.

Capacity of Carbon Dioxide

Figure 5 shows the measured and calculated effect of the pressure on the solubilities of 2-methylnaphthalene and hexadecane in supercritical carbon dioxide at a temperature of 80

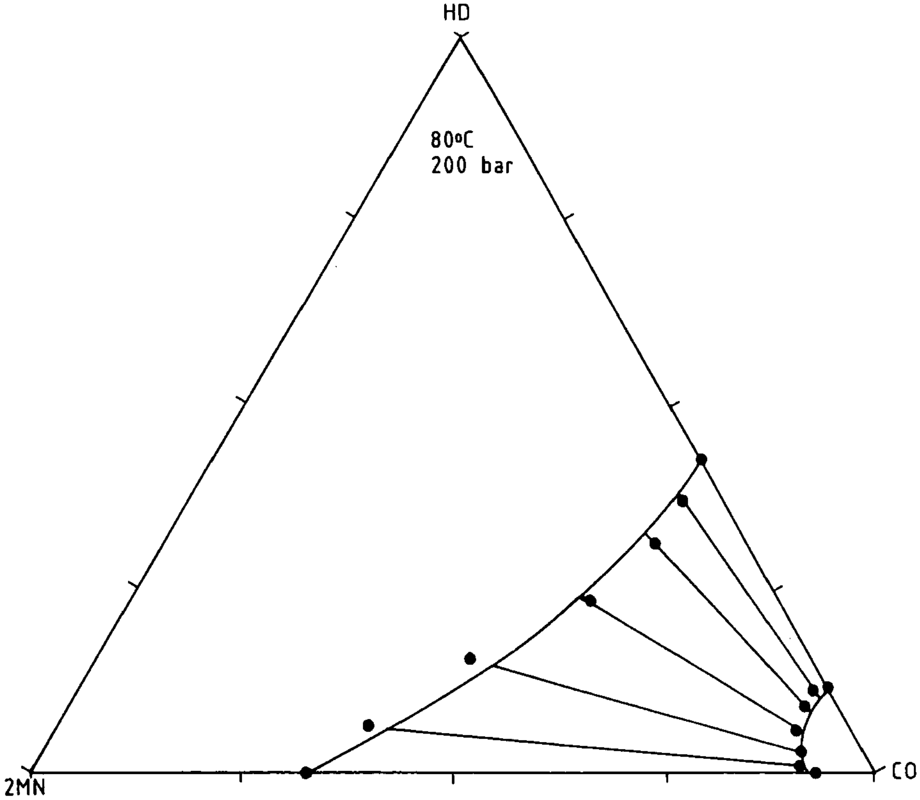

Fig.4. Measured (●) and calculated (-) vapour-liquid equilibria (%wt) of the model system 2-methyl-naphthalene/hexadecane/ carbon dioxide at 80 °C and 200 bar.

°C. If the pressure is increased the carbon dioxide density increases and the solubilities of 2-methylnaphthalene and hexadecane are increased markedly due to the stronger interactions between the carbon dioxide molecules and the 2-methylnaphthalene and hexadecane molecules.

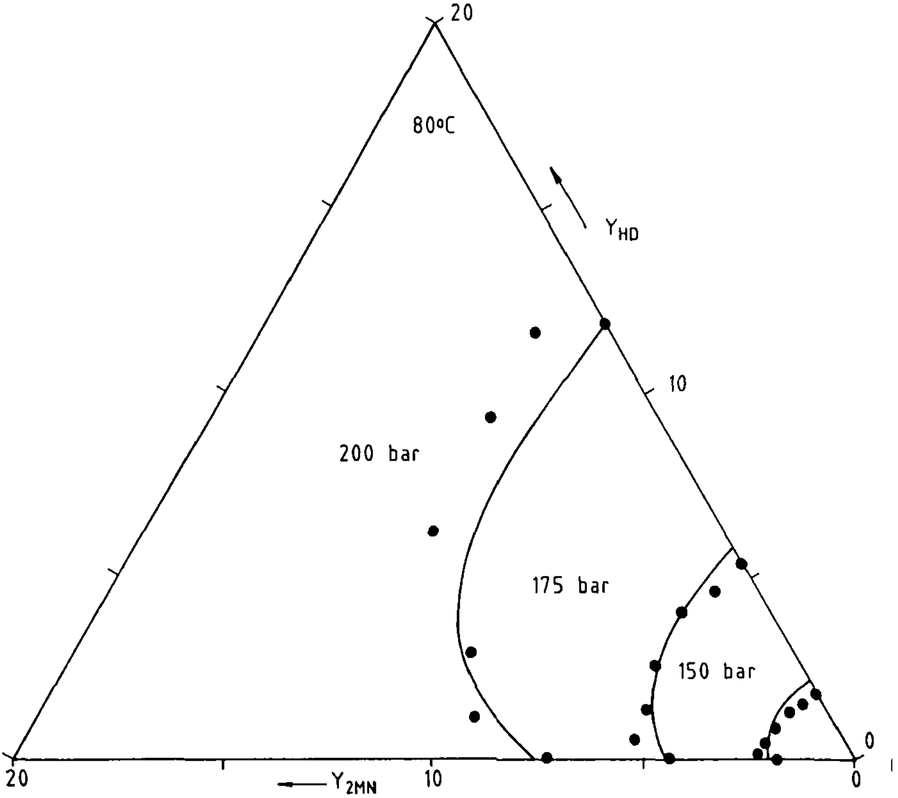

Fig.5. Measured (●) and calculated (-) solubility of 2-methylnaphthalene and hexadecane (%wt) in supercritical carbon dioxide as a function of pressure at 80 °C

The measured and calculated effect of the extraction temperature on the solubilities of 2-methylnaphthalene and hexadecane in supercritical carbon dioxide at a carbon dioxide density of 600 kg/m^3 is illustrated in figure 6. Increasing the extraction temperature from 50 to 80 °C results in higher solubilities of 2-methylnaphthalene and hexadecane in supercritical carbon dioxide due to the higher vapour pressures of both components (figure 1).

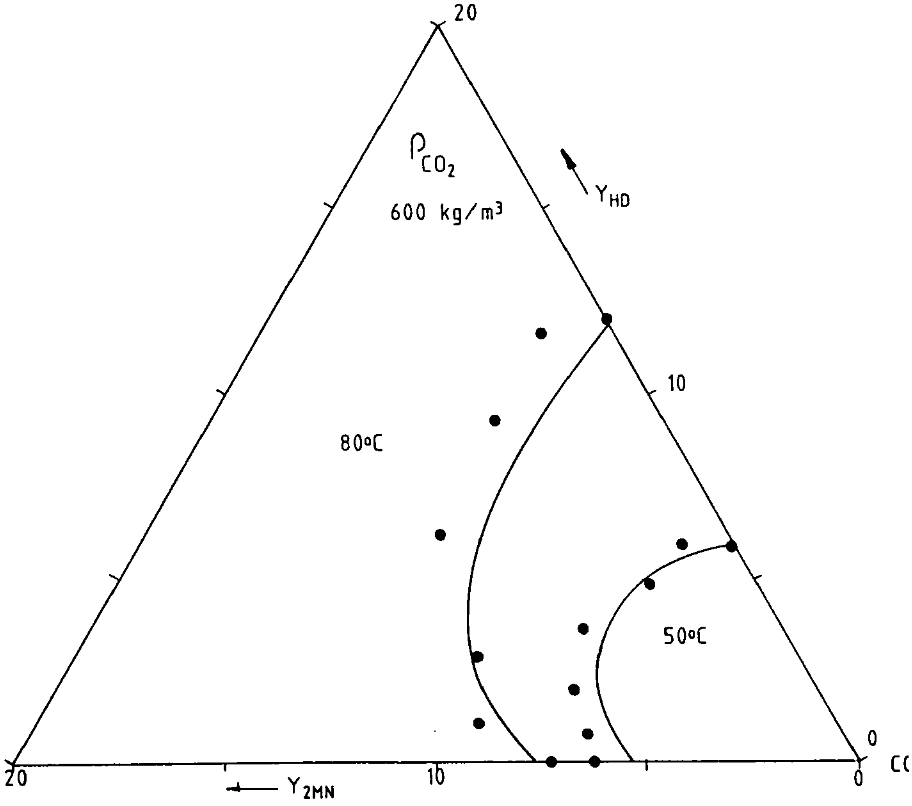

Fig.6. Measured (●) and calculated (-) solubility of 2-methylnaphthalene and hexadecane (%wt) in supercritical carbon dioxide as a function of temperature at a carbon dioxide density of 600 kg/m^3 (b).

Selectivity

Figure 7 shows the measured and calculated effect of the pressure and the 2-methylnaphthalene to hexadecane ratio in the liquid phase on the selectivity at a temperature of 80 °C. At low pressures the values of the selectivities indicate that 2-methylnaphthalene is more soluble in supercritical carbon dioxide than hexadecane due to the higher vapour pressure of 2-methylnaphthalene. When the carbon dioxide density is increased, the decrease in selectivity illustrates that the solubility of hexadecane in supercritical carbon dioxide increases more rapidly than the solubility of 2-methylnaphthalene. Furthermore it can be seen

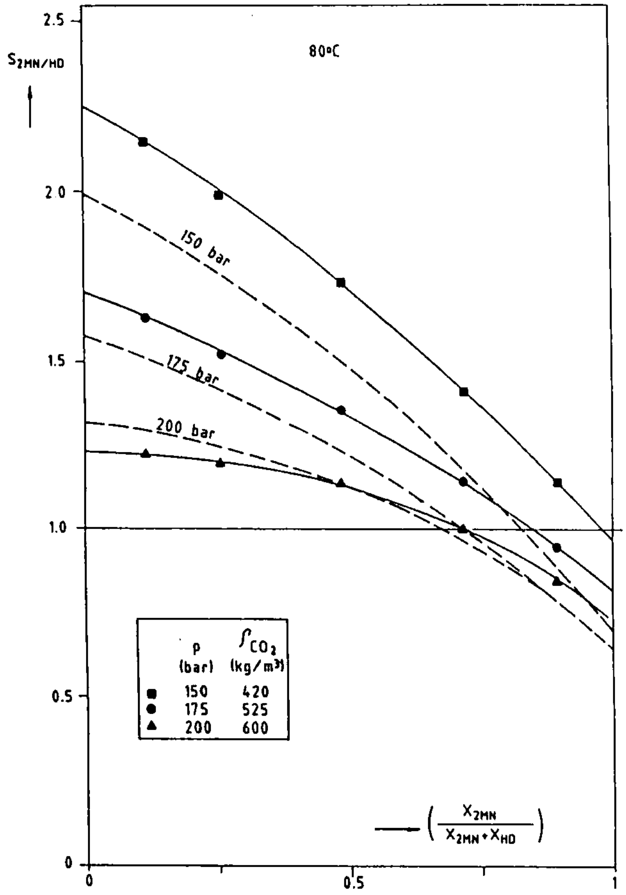

Fig.7. Measured (-■-,-●-,-▲-) and calculated (---) selectivity of supercritical carbon dioxide for 2-methylnaphthalene to hexadecane as a function of pressure and the ratio 2-methylnaphthalene and hexadecane in the liquid phase at 80 °C.

from figure 7 that the 2-methylnaphthalene to hexadecane ratio in the liquid phase has a large effect on the selectivity. This means that 2-methylnaphthalene and hexadecane form a non ideal liquid mixture in which the volatility of the components is largely dependent on the composition of the liquid phase.

Figure 8 illustrates the measured and calculated effect of the temperature on the selectivity. When the temperature is increased, the decrease in selectivity indicates that the solubility of hexadecane in supercritical carbon dioxide increases more rapidly than the solubility of 2-methylnaphthalene. This solubility behaviour can be explained since the vapour pressure of hexadecane rises more rapidly with temperature than the vapour pressure of 2-methylnaphthalene (figure 1).

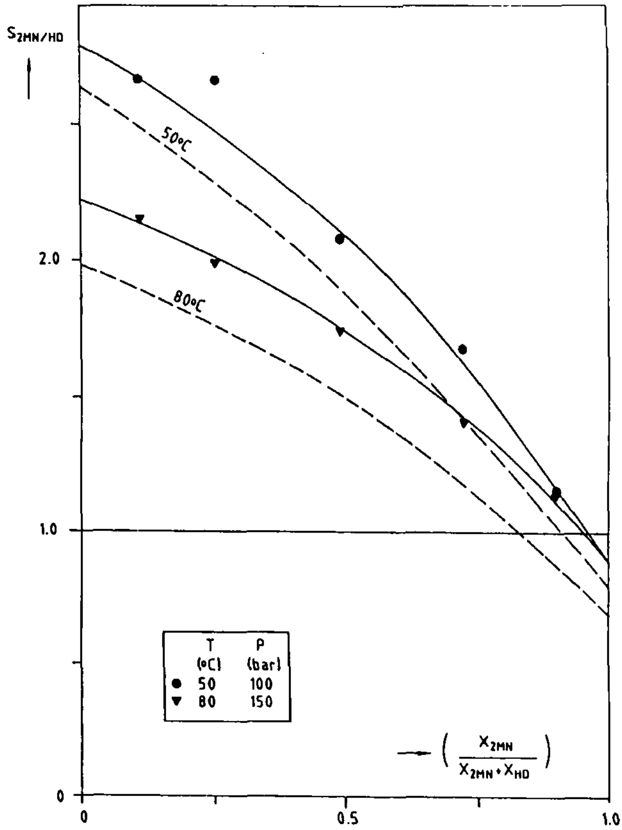

Fig.8. Measured (-●-,-▼-) and calculated (---) selectivity of supercritical carbon dioxide for 2-methylnaphthalene to hexadecane as a function of temperature and the ratio 2-methylnaphthalene and hexadecane in the liquid phase at a carbon dioxide density of 410 kg/m^3.

Figures 7 and 8 indicated that the selectivity of supercritical carbon dioxide originates mainly from the difference in vapour pressure between the alkanes and aromatics that are to be separated. This conclusion is confirmed when hexadecane is replaced by dodecane. The measured and calculated selectivities shown in figure 9 illustrate that in both model systems the component with the highest vapour pressure is more soluble in supercritical carbon dioxide. Therefore it can be concluded that the alkanes and aromatics are mainly separated on their difference in vapour pressure instead of their difference in chemical structure.

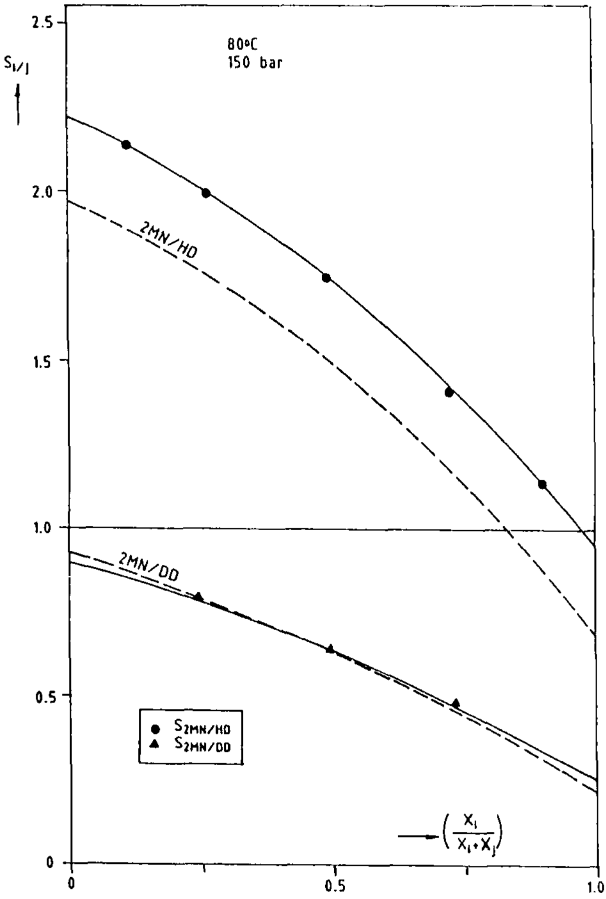

Fig.9. Measured and calculated (---) selectivity of supercritical carbon dioxide for 2-methylnaphthalene to hexadecane (-●-) and 2-methylnaphthalene to dodecane (-▲-) as a function of the ratio 2-methylnaphthalene/hexadecane and 2-methylnaphthalene/dodecane in the liquid phase at 80 °C and 150 bar.

CONCLUSIONS

A study to the separation of alkanes and aromatics with supercritical carbon dioxide has been made by measuring vapour-liquid equilibria and selectivities in the model systems 2-methylnaphthalene/hexadecane/carbon dioxide and 2-methylnaphthalene/dodecane/carbon dioxide. The results have been modelled with the Peng-Robinson equation of state.

From the obtained results it was concluded that supercritical carbon dioxide will separate alkanes and aromatics mainly on their difference in vapour pressure instead of their difference in chemical structure. Therefore supercritical carbon dioxide can only be used for specific applications where high boiling alkanes and aromatics are to be separated on basis of their relative volatility.

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LIST OF SYMBOLS

a	attraction parameter	(bar m^6 mol^{-2})
b	vd Waals covolume	(m^3 mol^{-1})
f	fugacity	(bar)
K	distribution coefficient	(-)
n	number of components	(-)
P	pressure	(bar)
S	selectivity	($S_{i/j}=Y_iX_j/Y_jX_i$)
T	temperature	(°C,K)
V	volume	(m^3)
x,X	liquid phase mole, weight fraction	(-)
y,Y	vapour phase mole, weight fraction	(-)

Greek Symbols

δ,η	binairy interaction parameters	(-)
ϕ	fugacity coefficient	(-)
ρ	density	(kg m^{-3})

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