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Separation of Alkanes and Aromatics with Supercritical C_2H_6, CO_2, $CClF_3$, and CHF_3

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Abstract

A study on the separation of alkanes and aromatics with supercritical ethane, carbon dioxide, monochlorotrifluoromethane, and trifluoromethane is presented. It appears that only with solvents that have a low dipole moment, such as ethane and carbon dioxide, can reasonable solubilities in the vapor phase be obtained. These low dipole moment solvents will separate alkanes and aromatics mainly on the basis of their difference in vapor pressure rather than on their difference in chemical structure. Therefore, supercritical solvents can only be used for specific applications where alkanes and aromatics have to be separated on the basis of their difference in vapor pressure.

Key Words: Supercritical extraction; Alkane aromatic separation

INTRODUCTION

The separation of alkanes and aromatics with polar solvents such as sulfolane or di- and triethylene glycol is one of the most important applications of liquid extraction in the petrochemical industry (*1*). In these liquid extraction processes most of the energy consumed is used for the separation of the extracted aromatics from the solvent. If a supercritical solvent could be used, this separation could simply be done in one step by pressure reduction. Therefore, the use of a supercritical solvent results in a much simpler process that may require less energy and investment capital.

From a previous study on the use of supercritical carbon dioxide for the separation of mixtures containing 2-methylnaphthalene and hexadecane or 2-methylnaphthalene and dodecane, we concluded that supercritical carbon dioxide will separate alkanes and aromatics mainly on basis of their difference in vapor pressures (*2*). In order to allow a further evaluation of the feasibility of supercritical fluid extraction, this paper presents the results of a study on the separation of alkanes and aromatics with supercritical

TABLE 1
Properties of the Model Components (*15*, *19*)

	T_c (K)	P_c (bar)	ω (—)	MW (g/mol)	μ (debye)
C_2H_6	305	48.8	0.099	30.1	0.0
CO_2	304	73.8	0.239	44.0	0.0
$CClF_3$	302	38.7	0.198	104.5	0.5
CHF_3	299	48.6	0.260	70.0	1.6
Dodecane	658	18.2	0.575	170.3	0.0
Hexadecane	734	15.3	0.742	226.4	0.0
2-Methylnaphthalene	761	35.0	0.382	142.3	0.4

ethane, carbon dioxide, monochlorotrifluoromethane, and trifluoromethane. These solvents have been selected because of their strong variation in dipole moment and yet nearly equal critical temperatures, as shown in Table 1. It is seen that ethane as well as carbon dioxide have no internal dipole moment. However, because carbon dioxide has an internal quadrupole moment, the studied solvents can be ordered by increasing dipole moment: ethane < carbon dioxide < monochlorotrifluoromethane < trifluoromethane. In this paper the effect of solvent–solute interactions on phase behavior, capacity, and selectivity has been studied. The results are modeled with the Peng–Robinson equation of state.

MODEL COMPONENTS

In our studies, 2-methylnaphthalene (aromatic) and hexadecane (alkane) were used as model components because their high boiling points make them difficult to separate from the solvents commonly used for the separation of alkanes and aromatics in liquid extraction processes. The phase behavior of ternary systems can be obtained by considering the three binary mixtures that comprise each ternary system. Parts of the *Px* isotherms for the binary systems hexadecane/carbon dioxide (*3*–*5*), 2-methylnaphthalene/carbon dioxide (*6*, *7*), hexadecane/ethane (*8*), and 2-methylnaphthalene/ethane (*9*, *10*) are available in the literature. No information could be found about the binary systems 2-methylnaphthalene/monochlorotrifluoromethane, 2-methylnaphthalene/trifluoromethane, hexadecane/trifluoromethane, hexadecane/monochlorotrifuloromethane, and 2-methylnaphthalene/hexadecane.

Figure 1 shows that 2-methylnaphthalene has a higher vapor pressure than hexadecane. The influence of the vapor pressures of the solutes on the selectivity and capacity was demonstrated by replacing hexadecane, with a lower vapor pressure than 2-methylnaphthalene, by dodecane that

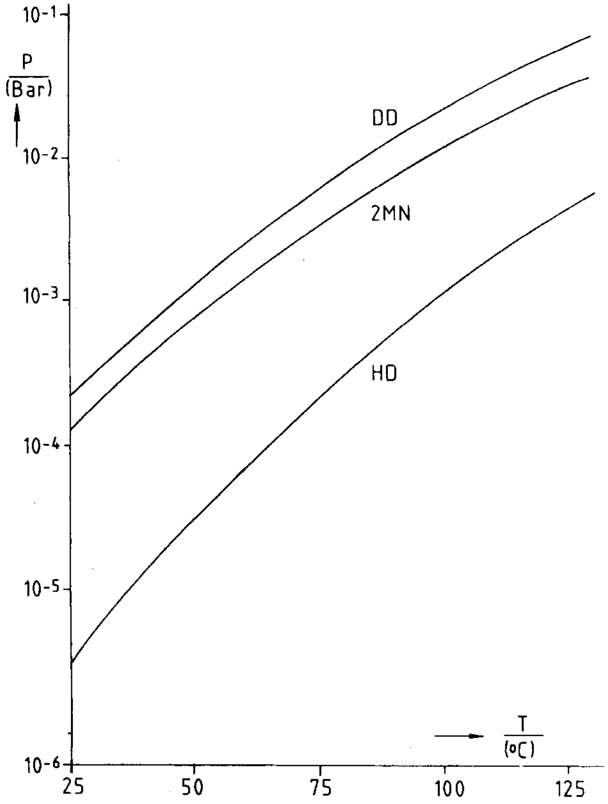


FIG. 1. Vapor pressure of dodecane (DD), 2-methylnaphthalene (2MN), and hexadecane (HD) as a function of the temperature (*15*).

has a higher vapor pressure than 2-methylnaphthalene. Parts of the *Px* isotherms for the binary systems dodecane/carbon dioxide (*11*, *12*) and dodecane/ethane (*13*) are available in the literature. No information was found for the binary systems dodecane/monochlorotrifluoromethane, dodecane/trifluoromethane, and dodecane/2-methylnaphthalene.

During our study it appeared that the data from the literature were insufficient to enable a good thermodynamic modeling of the phase equilibria required in this study. Therefore we decided to measure the required binary and ternary vapor–liquid equilibrium data ourselves, as described in the Experimental Section of this paper. Subsequently we have used our data to calculate the required binary interaction parameters.

CALCULATION OF VAPOR–LIQUID PHASE EQUILIBRIA

Vapor–liquid equilibria at high pressures are conveniently calculated by using an equation of state applicable to both phases (*14*, *15*). We have chosen to use the Peng–Robinson equation of state (*16*) because of its capability to represent high pressure vapor–liquid equilibria with reasonable accuracy (*14*) and because cubic equations of state are mathematically easy to handle:

$$P = \frac{RT}{v_m - b} - \frac{a(T)}{v_m(v_m + b) + b(v_m - b)} \tag{1}$$

For the pure components, $a(T)$ and b are calculated from the critical properties (Table 1):

$$a(T) = a(T_c)*\alpha(T) \tag{2}$$

$$a(T_c) = 0.45724(R^2T_c^2/P_c) \tag{3}$$

$$\alpha(T) = [1 + m(1 - (T/T_c)^{1/2})]^2 \tag{4}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

$$b = 0.07780(RT_c/P_c) \tag{6}$$

In a multicomponent mixture, $a(T)$ and b depend on the composition of the mixture and the interactions between the components (*15*). To account for the large differences in size, structure, and polarity between the molecules, the van der Waals mixing rules using two binary interaction parameters were claimed to be the most accurate (*17*):

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad (i, j = 1, 2, \ldots, n) \tag{7}$$

$$a_{ij} = (1 - \delta_{ij})(a_{ii}a_{jj})^{1/2} \tag{8}$$

and

$$b = \sum_i \sum_j x_i x_j b_{ij} \qquad (i, j = 1, 2, \ldots, n) \tag{9}$$

$$b_{ij} = (1 - \eta_{ij})(b_{ii} + b_{jj})/2 \tag{10}$$

TABLE 2
Calculated Binary Interaction Parameters

Components	δ_{ij}	η_{ij}
CO_2 + dodecane	0.09	0.06
CO_2 + hexadecane	0.08	0.03
CO_2 + 2-methylnaphthalene	0.07	−0.05
C_2H_6 + dodecane	—	—
C_2H_6 + hexadecane	−0.01	−0.02
C_2H_6 + 2-methylnaphthalene	0.00	−0.06
$CClF_3$ + dodecane	0.05	−0.04
$CClF_3$ + hexadecane	0.04	−0.05
$CClF_3$ + 2-methylnaphthalene	0.02	−0.07
CHF_3 + dodecane	0.22	0.00
CHF_3 + hexadecane	0.20	0.00
CHF_3 + 2-methylnaphthalene	0.05	−0.05
Dodecane + 2-methylnaphthalene	0.02	0.03
Hexadecane + 2-methylnaphthalene	0.00	0.02

The values of the binary interaction parameters δ_{ij} and η_{ij} were calculated from the vapor–liquid equilibrium data we measured during this study (*18*). For the solute/solvent systems we used the measured binary vapor–liquid equilibrium data. The solute/solute interactions were determined from the measured ternary *PTx* data. The optimal values for the interaction parameters, listed in Table 2, were determined by minimizing the relative error between the measured and calculated vapor and liquid phase compositions.

EXPERIMENTAL

A simplified flow sheet of the equipment used is shown in Fig. 2. The extraction column (4), with an internal diameter of 3.5 cm and a length of 1 m, was equipped with laboratory gauze packing (bed height 60 cm) and operated as a stripping column. The feed (1) entered the top of the column at extraction pressure (2) and extraction temperature (3). The remaining raffinate, containing considerable amounts (10–50 wt%) of solvent, was drawn off from the bottom of the column and expanded to 1 bar. A wet gas meter (11) was used to measure the amount of dissolved solvent, and the raffinate was drawn off periodically from the raffinate collection vessel (10). The supercritical solvent was fed to the bottom of the column at extraction pressure (8) and extraction temperature (9), and left the top of the column saturated with the dissolved extract. The pressure was reduced below the critical pressure of the solvent to condense the extract in the separator. This extract was drawn off periodically. The amount of solvent in which the extract was dissolved was calculated from the solvent flow to

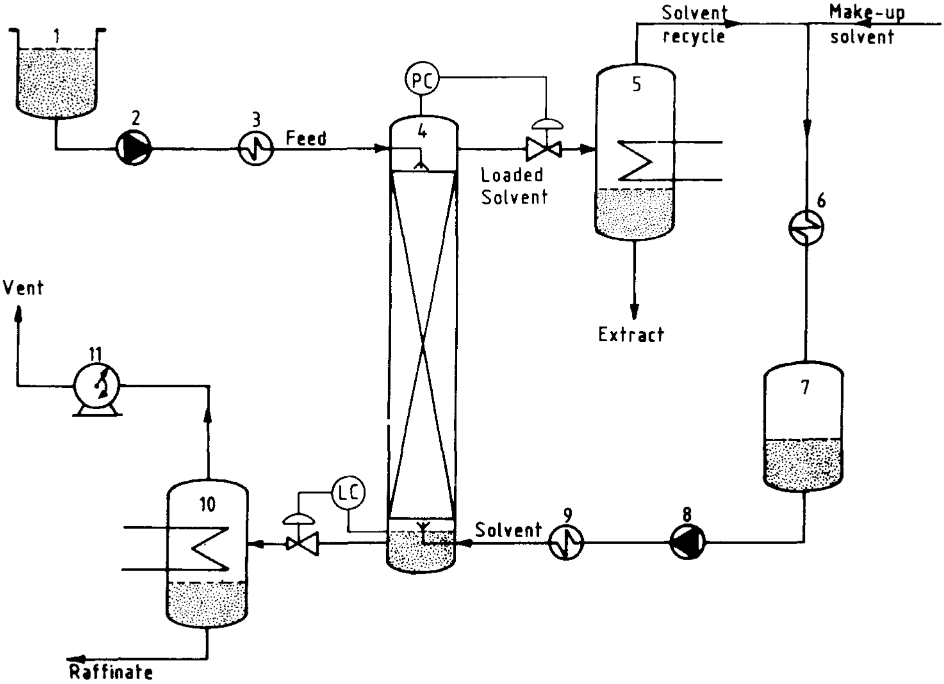


FIG. 2. Flow sheet of the supercritical extraction equipment. (1) Storage vessel, (2) pump, (3) heat exchanger, (4) column, (5) separator, (6) condensor, (7) CO_2 buffer vessel, (8) pump, (9) heat exchanger, (10) separator, (11) wet gas meter.

the column, measured with a Micro Motion mass flowmeter, by a solvent mass balance over the column. Fresh solvent was added to the evaporating solvent from the separator to compensate for losses in the raffinate. The gaseous solvent was subsequently 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 solvents. It appeared that under these conditions less than 10% of the feed was always extracted and that the extract stream leaving the column was in equilibrium with the liquid flowing down in the top of the column (*18*). The composition of this liquid was equal to the composition of the feed saturated with solvent. This amount of dissolved solvent was assumed to be equal to the amount of solvent dissolved in the raffinate that appeared to have nearly the same composition as the feed. The binary vapor–liquid equilibrium data for the solute/solvent systems were measured by contacting a feed of pure liquid hexadecane, 2-methylnaphthalene, or dodecane with a pure solvent. The binary system dodecane/ethane has not been measured because total miscibility was already obtained at a pressure around 70 bar. In the case of the ternary systems the vapor–liquid equilibrium data were measured by contacting a feed containing a mixture of hexadecane and 2-methylnaphthalene or dodecane and 2-methylnaphthalene with a pure solvent. The compositions of the solvent-free feed and the collected solvent-free raffinate and solvent-free extract, containing a mixture of 2-methylnaphthalene and hexadecane or 2-methylnaphthalene and dodecane, were measured with a refractometer. The ternary system 2-methylnaphthalene/dodecane/ethane was not measured because the binary system dodecane/ethane could not be measured.

Except for the measurements with ethane, the average relative variation of the measured weight fractions of the separate components in the vapor and liquid phase appeared to be about 5%. In the case of ethane the low density in the mass flowmeter, that is only suited for liquidlike densities, resulted in an average relative variation of about 10% in the vapor phase composition. The average relative variation in the liquid phase composition remained about 5% because the ethane solubility in the liquid phase was measured directly with the wet gas meter.

The dodecane, >99% purity, was obtained from Jansen Chimica. The hexadecane, >99% purity, and the 2-methylnaphthalene, >96% purity, were products from Merck-Schuchardt. Hoek-Loos supplied the >99.99% pure carbon dioxide. The ethane, >99.5% purity, monochlorotrifluoromethane, >99% purity, and the trifluoromethane, >99% purity, were obtained from Air Products. All these materials were used without further purification.

RESULTS

The vapor–liquid equilibrium data we measured and used for this study can be found elsewhere (*18*).

Phase Behavior

The measured and calculated phase behaviors of the ternary mixtures of 2-methylnaphthalene and hexadecane with ethane, carbon dioxide, monochlorotrifluoromethane, and trifluoromethane at a solvent-based reduced pressure of 2.05 and a solvent-based reduced temperature of 1.17 (80°C) are shown in Figs. 3(a) to 3(d). It is seen that the solubility of the solvents in the liquid phase decreases in the order ethane > carbon dioxide > monochlorotrifluoromethane > trifluoromethane, corresponding to the increasing dipole moment of the solvents. This effect of increasing dipole

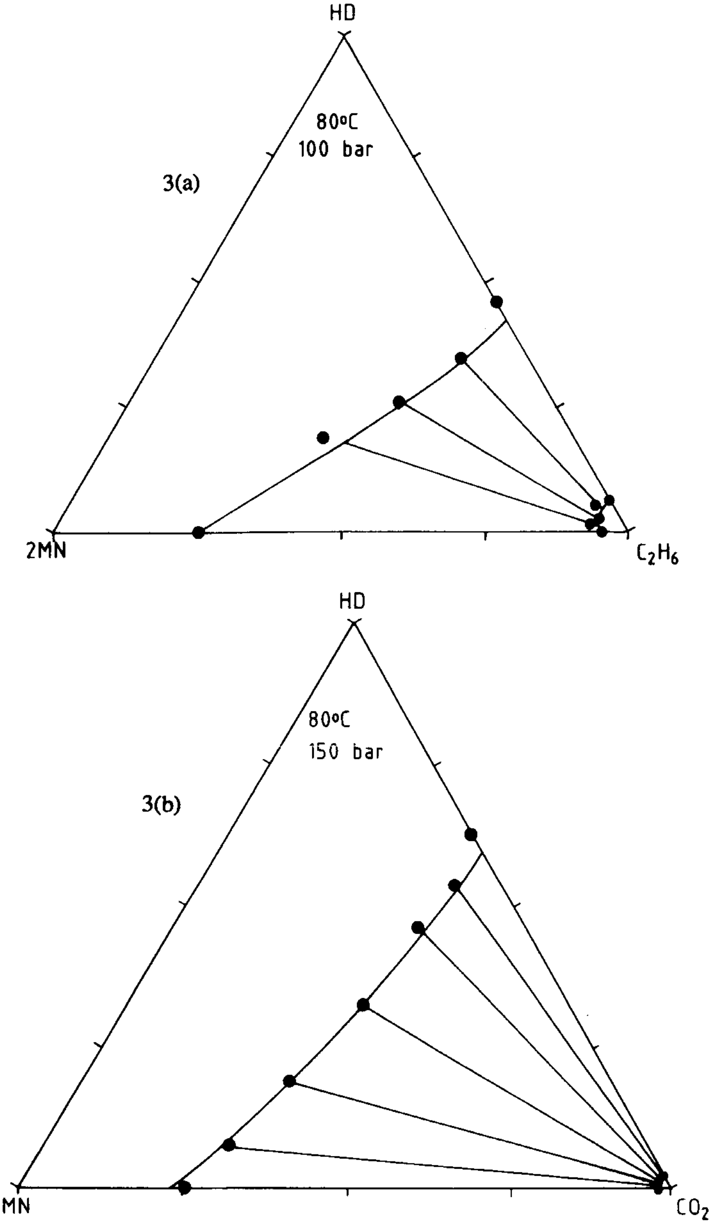
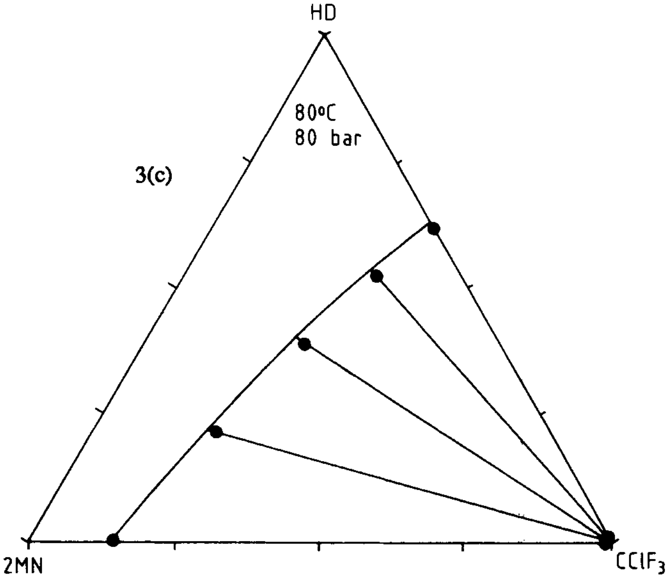


FIG. 3. Measured (●) and calculated (——) phase behavior (wt%) of ternary mixtures of 2-methylnaphthalene and hexadecane with ethane (a), carbon dioxide (b), monochlorotrifluoromethane (c), and trifluoromethane (d) at a solvent-based reduced pressure of 2.05 and a solvent-based reduced temperature of 1.17. (a) $P_{r,C_2H_6} = 2.05$, $T_{r,C_2H_6} = 1.16$; (b) $P_{r,CO_2} = 2.03$, $T_{r,CO_2} = 1.16$; (c) $P_{r,CClF_3} = 2.06$, $T_{r,CClF_3} = 1.17$; (d) $P_{r,CHF_3} = 2.06$, $T_{r,CHF_3} = 1.18$.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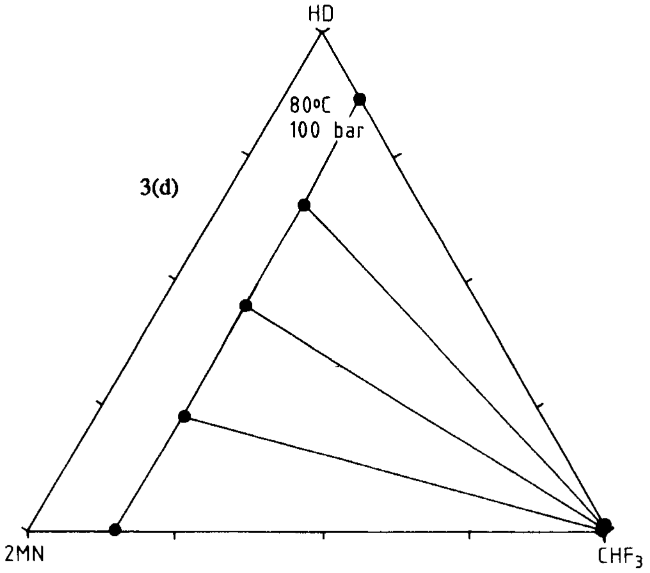
80°C
80 bar
3(c)
2MN
CClF$_3$


HD
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3(d)
2MN
CHF$_3$

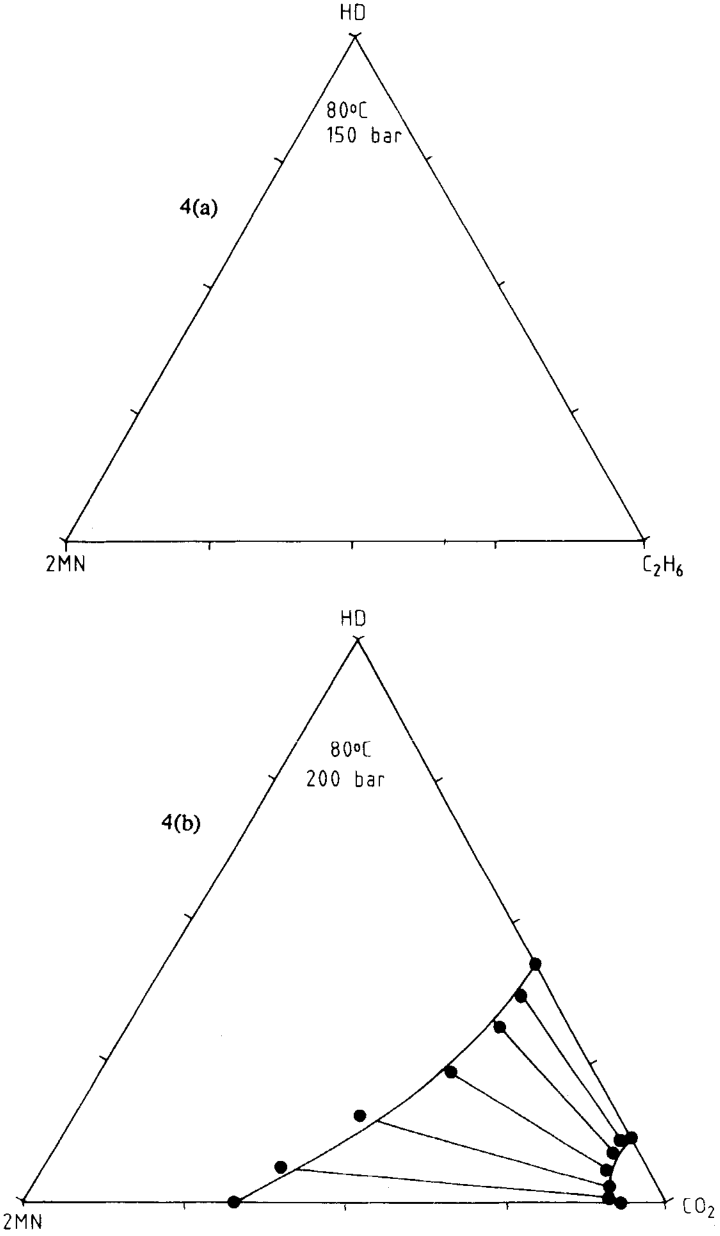
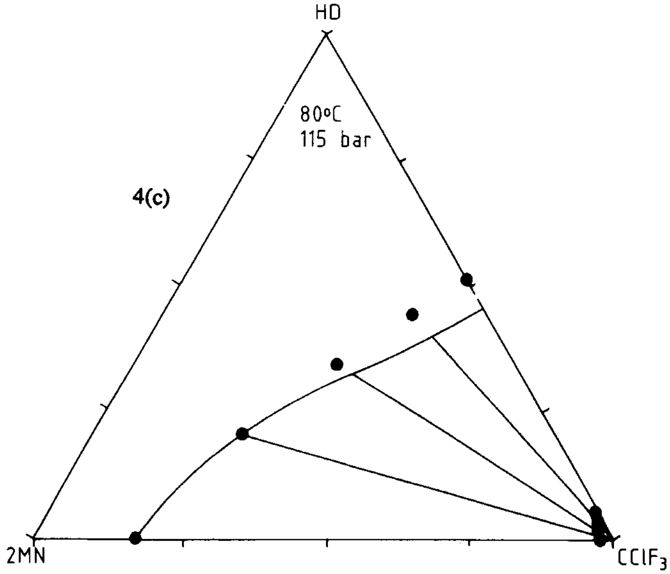
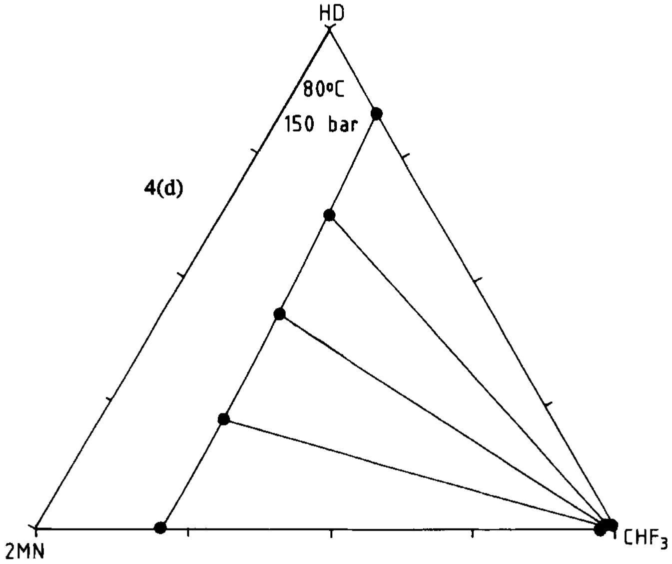


FIG. 4. Measured (●) and calculated (——) phase behavior (wt%) of ternary mixtures of 2-methylnaphthalene and hexadecane with ethane (a), carbon dioxide (b), monochlorotrifluoromethane (c), and trifluoromethane (d) at a solvent-based reduced pressure of about 3.0 and a solvent-based reduced temperature of 1.17. (a) $P_{r,C_2H_6} = 3.07$, $T_{r,C_2H_6} = 1.16$; (b) $P_{r,CO_2} = 2.71$, $T_{r,CO_2} = 1.16$; (c) $P_{r,CClF_3} = 2.97$, $T_{r,CClF_3} = 1.17$; (d) $P_{r,CHF_3} = 3.08$, $T_{r,CHF_3} = 1.18$.



4(c)



4(d)

moment was also measured for the solubility of 2-methylnaphthalene and hexadecane in the vapor phase that increases in the same order.

When the reduced pressure is raised from 2.05 to around 3.0, Fig. 4(a) shows that complete miscibility of the 2-methylnaphthalene/hexadecane/ethane system has already been obtained, resulting mainly from the increased liquid phase solubility of ethane. Figures 4(b) to 4(d) illustrate that the concentration of the other three solvents in the liquid phase also increases with higher reduced pressures. This effect of reduced pressure on the liquid phase solubility decreases in the order ethane > carbon dioxide > monochlorotrifluoromethane > trifluoromethane, and it is consistent with the increasing dipole moment of the solvents. Furthermore, it is seen from Figs. 4(b) to 4(d) that the solubility of 2-methylnaphthalene and hexadecane in the vapor phase has increased markedly at a higher reduced pressure. This solubility enhancement of the vapor phase was also found to increase according to the order ethane > carbon dioxide > monochlorotrifluoromethane > trifluoromethane.

Solvent Capacity

The capacity of a supercritical solvent is mainly controlled by the solvent density, the temperature, and the affinity of the solvent for the solutes. In our previous study (*2*) we showed that the hexadecane and 2-methylnaphthalene solubility in supercritical carbon dioxide increases with increasing pressure at a fixed temperature. Furthermore, it appeared that hexadecane and 2-methylnaphthalene solubility also increased with increasing temperatures when the carbon dioxide density was kept constant. The measurements performed for this study showed that the effect of pressure and temperature on the capacity is qualitatively the same for the four solvents studied. Therefore, only the effect of solvent affinity on the solubility of the solutes will be discussed here by considering the measured and calculated solubility of 2-methylnaphthalene and hexadecane in supercritical ethane, carbon dioxide, monochlorotrifluoromethane, and trifluoromethane at a solvent-based reduced pressure of 2.05 and a solvent-based reduced temperature of 1.17 (80°C) shown in Fig. 5. It is seen that the solubility decreases rapidly with increasing solvent dipole moment according to the order ethane > carbon dioxide > monochlorotrifluoromethane > trifluoromethane. Therefore, it can be concluded that of the solvents studied, only ethane and carbon dioxide have enough affinity for nonpolar components such as alkanes and aromatics to obtain sufficiently high solubilities.

Selectivity

The selectivity of a supercritical solvent in a given system is determined by the solvent density, the temperature, the composition of the liquid

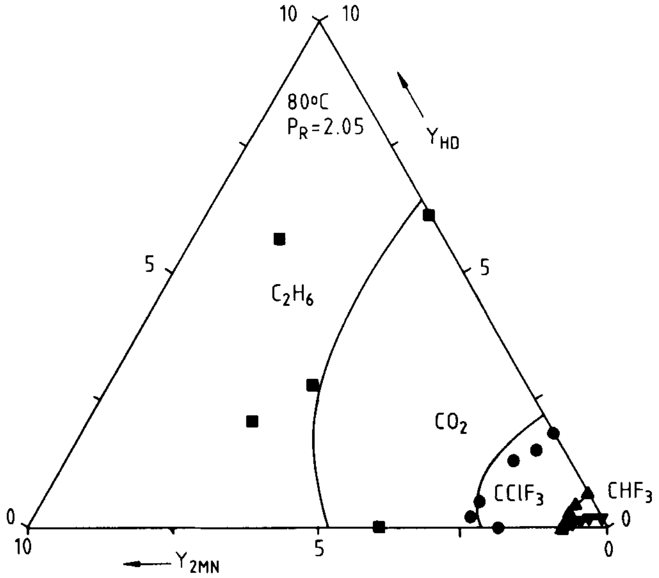


FIG. 5. Measured and calculated (——) solubility of 2-methylnaphthalene and hexadecane (wt%) in supercritical ethane (■) (100 bar), carbon dioxide (●) (150 bar), monochlorotrifluoromethane (▲) (80 bar), and trifluoromethane (▼) (100 bar) at a solvent-based reduced pressure of 2.05 and a solvent-based reduced temperature of 1.17 (80°C).

phase, and the difference in affinity for the solutes. In our previous paper (*2*) we demonstrated that supercritical carbon dioxide will separate alkanes and aromatics mainly on the basis of their difference in vapor pressure since dodecane was extracted from a dodecane/2-methylnaphthalene mixture while 2-methylnaphthalene was extracted from a hexadecane/2-methylnaphthalene mixture. The selectivities obtained decreased with increasing pressure and increasing temperature. From the experiments performed for this study it appeared that for other three solvents the selectivities obtained also decreased with increasing pressure and increasing temperature. For this reason only the effect of solvent affinity on the selectivity will be discussed in this paper. For the model systems studied, the selectivity of a solvent for solute *i* over solute *j* has been defined as

$$S_{i/j} = \frac{K_i}{K_j} = \frac{Y_i}{Y_j} * \frac{X_j}{X_i} \qquad (11)$$

When carbon dioxide is replaced by other solvents, a higher selectivity for the aromatic or the alkane might be obtained. The measured and calculated selectivities of ethane, carbon dioxide, monochlorotrifluoromethane, and trifluoromethane for 2-methylnaphthalene to hexadecane at a solvent-based reduced pressure of 2.05 and a solvent-based reduced temperature of 1.17 (80°C) are plotted in Fig. 6. It is seen that only with trifluoromethane is a much higher selectivity for 2-methylnaphthalene obtained. This indicates that while ethane, carbon dioxide, and monochlororotrifuloromethane will separate 2-methylnaphthalene and hexadecane mainly on the basis of their difference in vapor pressure, trifluoromethane separates them more on the basis of their difference in chemical structure.

Replacing hexadecane with dodecane results in the measured and cal-

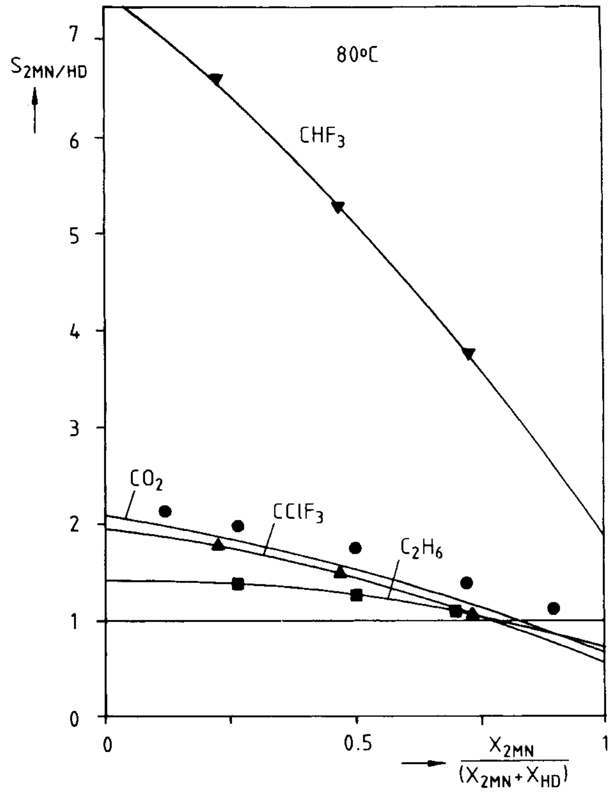


FIG. 6. Measured and calculated (——) selectivity of supercritical ethane (■) (100 bar), carbon dioxide (●) (150 bar), monochlorotrifluoromethane (▲) (80 bar), and trifluoromethane (▼) (100 bar) for 2-methylnaphthalene to hexadecane as a function of the ratio of 2-methylnaphthalene to hexadecane in the liquid phase at a solvent-based reduced pressure of 2.05 and a solvent-based reduced temperature of 1.17 (80°C).

culated selectivities of trifluoromethane for 2-methylnaphthalene shown in Fig. 7. It is seen that the selectivity of trifuoromethane for 2-methylnaphthalene in a mixture of 2-methylnaphthalene and dodecane has decreased dramatically. This decreased selectivity results mainly from the much higher vapor pressure of dodecane compared to hexadecane (*2*). Furthermore, Fig. 7 illustrates that it is impossible to separate a mixture of 2-methylnaphthalene and dodecane into its pure components because this system contains a solutrope as a result of the decreased selectivity. Therefore, it can be concluded that, although solvents with a high dipole moment such as trifluoromethane show an affinity for the aromatic structure, the selectivities obtained are not high enough to separate complex

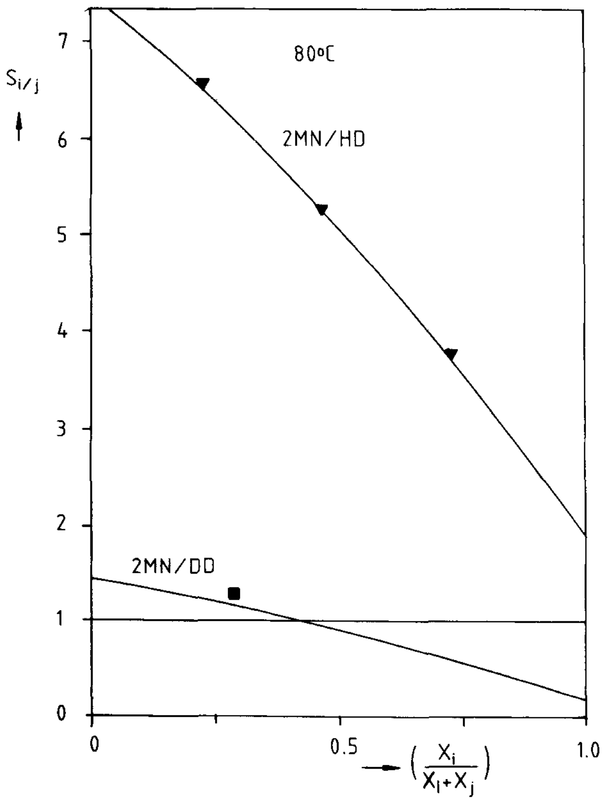


FIG. 7. Measured and calculated (——) selectivity of supercritical trifluoromethane for 2-methylnaphthalene to hexadecane (▼) and 2-methylnaphthalene to dodecane (■) as a function of the ratio of 2-methylnaphthalene to hexadecane and 2-methylnaphthalene to dodecane in the liquid phase of 80°C and 100 bar.

mixtures of alkanes and aromatics with overlapping boiling points on the basis of their difference in chemical structure. Moreover, the solubility of hydrocarbons such as alkanes and aromatics in supercritical solvents with a high dipole moment will be very low (Fig. 5), resulting in processes that are highly uneconomical due to the huge amounts of solvent required.

Modeling

Figure 3(a) to 3(d) and 4(a) to 4(d) show that the Peng–Robinson equation of state can be used to generate a reasonable representation of the phase behavior in the alkane/aromatic/supercritical solvent systems studied. The solubility of hexadecane and 2-methylnaphthalene in supercritical ethane, carbon dioxide, monochlorotrifluoromethane, and trifluoromethane (Fig. 5) was calculated reasonably well. As far as the selectivities are concerned, the calculated behavior is less in agreement with the experimental data. Although not directly visible in Figs. 6 and 7, it appeared during the optimization calculations that the Peng–Robinson equation of state faced difficulties in getting the calculated selectivities in agreement with the measured data because small deviations between the measured and calculated vapor and liquid phase compositions resulted in much larger deviations between the measured and calculated selectivities.

CONCLUSIONS

A study on the separation of alkanes and aromatics with supercritical solvents has been carried out by measuring vapor–liquid equilibria and selectivities for mixtures of 2-methylnaphthalene and hexadecane with supercritical ethane, carbon dioxide, monochlorotrifluoromethane, and trifluoromethane. These solvents have been selected because of their strong variation in dipole moment and yet almost equal critical temperatures. The results have been modeled with the Peng–Robinson equation of state that appears capable of representing vapor and liquid phase compositions of the experimental data with reasonable accuracy. The representation of the selectivity data, however, was less in agreement with the experimental data because small deviations between the measured and calculated vapor and liquid phase compositions resulted in much larger deviations between the measured and calculated selectivities.

The experimental results obtained indicated that only with trifluoromethane, which has a high dipole moment, can a much higher selectivity for 2-methylnaphthalene be obtained. For practical applications, however, the affinity of trifluoromethane for the aromatic structure is not high enough to be able to separate complex mixtures of alkanes and aromatics with overlapping boiling points on their difference in chemical structure.

Furthermore, it appears that the solubility of 2-methylnaphthalene and hexadecane in the supercritical solvents studied decreases rapidly in the order ethane > carbon dioxide > monochlorotrifluoromethane > trifluoromethane, corresponding to the increasing dipole moments of the solvents. In the case of trifluoromethane, the very low solubilities obtained would result in highly uneconomical processes due to the huge amounts of solvent required.

In general, it can be concluded that only with supercritical solvents that have a low dipole moment, such as ethane and carbon dioxide, can sufficiently high solubilities of nonpolar hydrocarbons such as alkanes and aromatics be obtained. These solvents will separate alkanes and aromatics mainly on their difference in vapor pressure rather than on their difference in chemical structure. Therefore, they can only be used for specific applications where high boiling alkanes and aromatics are to be separated on the basis of their relative volatilities.

NOTATION

a	attraction parameter (bar·m^6·mol^{-2})
b	van der Waals covolume (m^3/mol)
MW	molecular weight (g/mol)
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	liquid-phase mole fraction (—)
X	liquid-phase weight fraction (—)
y	vapor-phase mole fraction (—)
Y	vapor-phase weight fraction (—)

Greek Letters

δ	binary interaction parameter (—)
η	binary interaction parameter (—)
μ	dipole moment (debye)
ω	acentric factor (—)
ρ	density (kg/m^3)

Super- and Subscripts

c	critical
i	component

j	component
m	molar
r	reduced

Acknowledgments

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