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Supercritical Chromatography of Paraffins on a Molecular Sieve: Analytical and Preparative Scale

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Abstract

Supercritical carbon dioxide has been used as the mobile phase in chromatographic investigations of higher paraffins on molecular sieve 5A at temperatures from 40 to 200°C and pressures up to 20 MPa. The pressure and temperature dependence of retention data of paraffins up to eicosane found experimentally are discussed and compared with results of model calculations. Furthermore, some physicochemical applications of the high pressure retention data seem to be possible. A pressure-programmed group separation process permitting analytical and preparative scale separations of *n*- and isoparaffin mixtures is outlined.

INTRODUCTION

The outstanding solvent power of supercritical fluids was demonstrated by Villard (*1*) in 1898; he observed that paraffins were completely dissolved by compressed ethylene at 20°C and 15 MPa. Zosel (*2*) first applied supercritical ethylene as a mobile phase in chromatographic separations of paraffins at ambient temperature in 1965. Detailed investigations of the chromatographic behavior of *n*-paraffins up to C_{12} in compressed carbon dioxide were carried out by Bartmann and Schneider (*3*). Besides the chromatographic separation effect, they also investigated the physicochemical fundamentals of the *n*-paraffin/CO_2 system. Liphard and Schneider (*4*) carried out similar investigations for squalane (chain length C_{30}) in CO_2.

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An interesting new aspect is the application of supercritical chromatography to group separation of *n*- and isoparaffins of higher chain length, commonly carried out on molecular sieve 5A. The selectivity of this separation is based on the sieve effect, i.e., the *n*-paraffins are strongly retained in the cavities of the molecular sieve while the isoparaffins pass through the adsorption bed nearly unretarded. As is well known, desorption of *n*-paraffins needs extreme conditions: either high temperatures or long elution times. Therefore, in analytical practice, after the elution of the isoparaffins from molecular sieve 5A, the *n*-paraffins are determined either by pyrolysis in the column at temperatures beyond 400°C (*5*) or by backflushing to the column entrance (*6*).

In industrial scale separations of *n*- and isoparaffin fractions, the desorption of *n*-paraffins from the molecular sieve is carried out in three different ways (*7–9*): (a) in the vapor phase using a displacing agent (PAREX process), (b) in the liquid phase using liquid elution agents (MOLEX process), (c) by means of vacuum without any elution agent (pressure swing processes).

A new method where the *n*-paraffins are eluted from molecular sieve 5A by means of supercritical CO_2 was presented in our earlier work (*10*). In this approach the chromatographic behavior of *n*- and isoparaffins was investigated as a function of the CO_2 pressure between 0.5 and 20 MPa at temperatures between ambient and 200°C (*11*). Following this preliminary survey, both analytical and preparative group separations of *n*- and isoparaffins at mild thermal conditions were undertaken (*14*).

ANALYTICAL SCALE CHROMATOGRAPHY

Experimental

A gas-chromatograph GCHF 18.3/4 (VEB Chromatron Berlin, DDR) was modified for application to supercritical chromatography (Fig. 1). A specially developed detector module containing a flame ionization detector (FID) (Chromatron) connected with a splitting valve (Nupro fine metering needle valve) was installed. In order to avoid condensation of the effluent after expansion, the line connecting the FID with the column was shortened and its inner diameter was reduced to 0.16 mm by inserting a capillary to increase the gas velocity.

The FID was operated in the split mode; the typical split ratio is 1:100.

The carrier gas was fermentation CO_2, dried and purified by means of

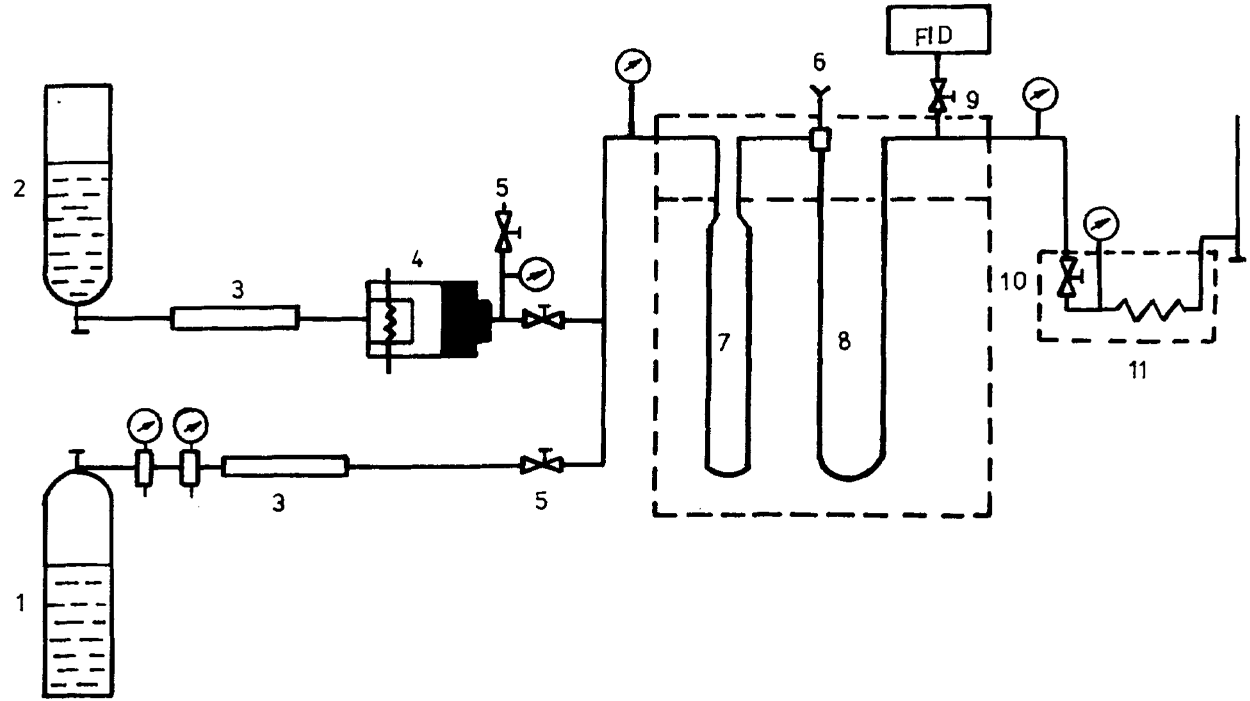

FIG. 1. Apparatus for analytical supercritical chromatography: (1, 2) CO_2 pressure cylinders, (3) molecular sieve drying cartridge, (4) micrometering pump MC 300 with Peltier battery, (5) combination of needle valves for pressure programming, (6) injection port, (7) temperature stabilization capillary, (8) column, (9) splitting valve, (10) expansion needle valve, (11) flowmeter.

molecular sieves 4A and 13X, and containing N_2 and O_2 ($\leqslant 0.2\%$) as impurities.

For compression of the mobile phase a modified micrometering pump MC 300 (Mikrotechna Praha, CSSR) was used. The pump head was cooled to −10°C by a Peltier battery. The ballistic pressure program was carried out by a combination of needle valves (Whitey fine metering valves) which are used as shut-off valves for switching the gas streams from the low-pressure to the high-pressure part of the carrier gas delivery unit and for rapid expansion to atmosphere after a pressure programmed cycle.

The column consists of a 50-cm stainless steel tube with an internal diameter of 3 mm. The sample was injected by a Valvseal septumless injector (Precision Sampling Corporation, Baton Rouge, Louisiana).

The different parts of the apparatus were connected by stainless steel capillary, 0.2 mm i.d.

The flow rate of the carbon dioxide used as the carrier fluid was 60 L/h NPT (20°C, 760 torr). Both pressure and flow of the carrier gas are controlled by an in-house manufactured expansion needle valve which is manually controlled and thermostated to 75°C to avoid condensation effects.

Molecular sieve 5A (particle size 0.16–0.20 mm) was used as the stationary phase. It was filled by tapping and vibrating the column and preconditioned by heating to 250°C under a carrier gas stream for 3 h.

Discussion of the Analytical Results

Pressure Dependence of the Retention Data

With CO_2 at pressures ranging from 4 to 12 MPa, *n*-paraffins of chain lengths up to C_{14} can be rapidly eluted at 40°C as shown in Fig. 2, which presents retention time as a function of CO_2 pressure for six compounds.

Similar short retention times with conventional carrier gases on a molecular sieve 5A column require temperatures above 400°C where considerable amounts of *n*-paraffins are decomposed. However, at low column temperatures *n*-paraffins with more than 14 carbon atoms elute more slowly, resulting in profiles that are unsuitable for good qualitative and quantitative interpretation. The diffuse elution profiles obtained under these conditions are obviously not due to the strong adsorption effect of the molecular sieve but to the common influence of the three effects—pressure, temperature, and solute vapor pressure—on the CO_2/

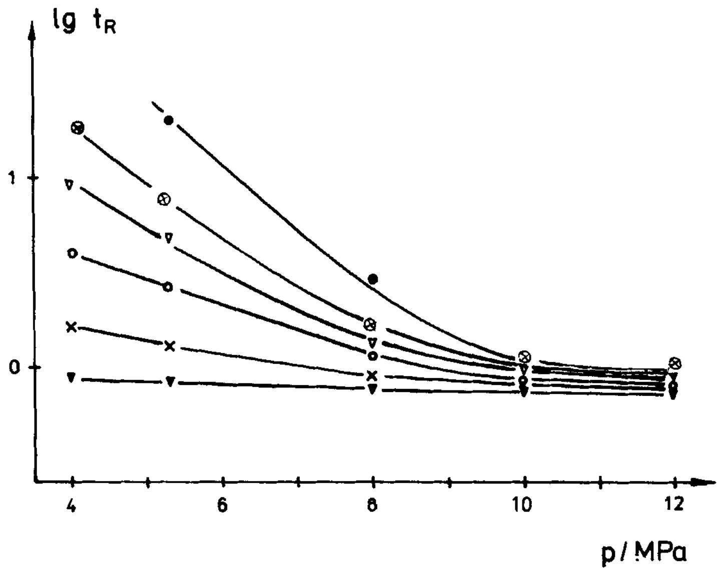

FIG. 2. Pressure dependence of the retention time of *n*-paraffins. Column temperature = 40°C, t_R in minutes. (▼) *n*-Nonane, (X) *n*-decane, (O) *n*-undecane, (∇) *n*-dodecane, (⊗) *n*-tridecane, (●) *n*-tetradecane.

paraffin phase equilibrium. The temperature dependence of the adjustment of the sorption equilibrium should be of increasing influence on the retention data. Therefore, in order to decrease the retention time of the higher molecular weight substances, it is necessary to optimize both the pressure and the column temperature to attain a sufficiently high solute vapor phase concentration.

As shown in Fig. 2, the retention volumes decrease with increasing pressure, approaching the dead volume of the column. The separation coefficients of neighboring paraffins, $\alpha = t_{n+1}/t_n$, closely approaches 1, conveniently permitting the elution of the *n*-paraffins investigated as a compact chromatographic peak for the group separation process used.

Furthermore, increasing the temperature from 40 to 100°C made it possible to elute *n*-paraffins up to eicosane with sharp elution curves from molecular sieve 5A at a pressure of 8 MPa.

Estimation of the Partition Coefficients

At the present time a satisfactory theoretical description of the fluid state is impossible. However, within a limited pressure range up to 5 MPa the pressure dependence of the partition coefficient of Component 2 dissolved in carbon dioxide can be described by the relation

$$K_2 = \frac{p}{p_{02}} \exp (p - p_{02}) \frac{(B_{22} - v_{02} + \Delta_{12})}{RT} \tag{1}$$

where $\Delta_{12} = 2B_{12} - (B_{11} + B_{22})$

p = pressure
p_{02} = vapor pressure of pure Component 2
B = second virial coefficient
v_{02} = molar volume of pure Component 2
R = gas constant
T = temperature

The partition coefficients calculated by Eq. (1) as a function of pressure for 2,4-dimethylheptane, *n*-nonane, and *n*-tridecane are shown in Fig. 3. Corresponding values obtained by SFC are indicated by the black circles in Fig. 3.

The similar shape and position of the curves seems to demonstrate that the supercritical solvent effect essentially determines the pressure dependence of the partition coefficients. However, the experimentally measured partition coefficients are considerably smaller than the calculated K values. Obviously this deviation is caused by the influence of the molecular sieve properties on K which is neglected in Eq. (1).

A better adaption to the experimental values seems to be achieved by multiplying Eq. (1) by a semiempirical coefficient that is a function of the transport coefficient D_a of the paraffins in the molecular sieve:

$$K_2 = \frac{p}{p_{02}} \exp (p - p_{02}) \frac{(B_{22} - v_{02} + \Delta_{12})}{RT} \exp (-112 D_a) \tag{2}$$

The curve obtained by Eq. (2) is given by the broken lines in Fig. 3. As expected, the K values obtained by Eq. (2) are significantly lower, thus providing a good correspondence with the values obtained chromatographically.

A more detailed discussion of the empirical coefficient in Eq. (2) will be possible only after further investigation of molecular sieve types. Using Eq. (2) it should be possible to characterize the separation properties of different molecular sieves in supercritical chromatography.

In Fig. 4 the experimental $K_{\max}$ values of some *n*-paraffins are compared with the values calculated by Eqs. (1) and (2).

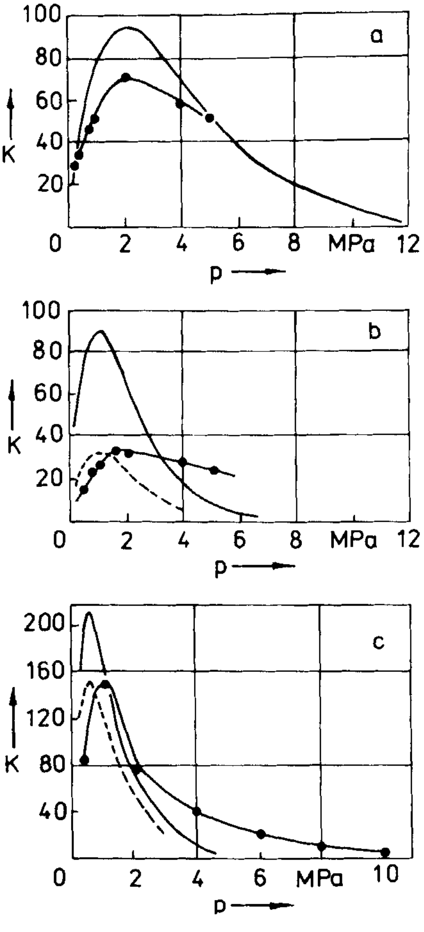

FIG. 3. Pressure dependence of the partition coefficients with column temperature = 60°C: (——) calculated by Eq. (1), (- -) calculated by Eq. (2), (•) experimental values obtained by SFC. (a) 2,4-Dimethylheptane; (b) *n*-nonane; (c) *n*-tridecane.

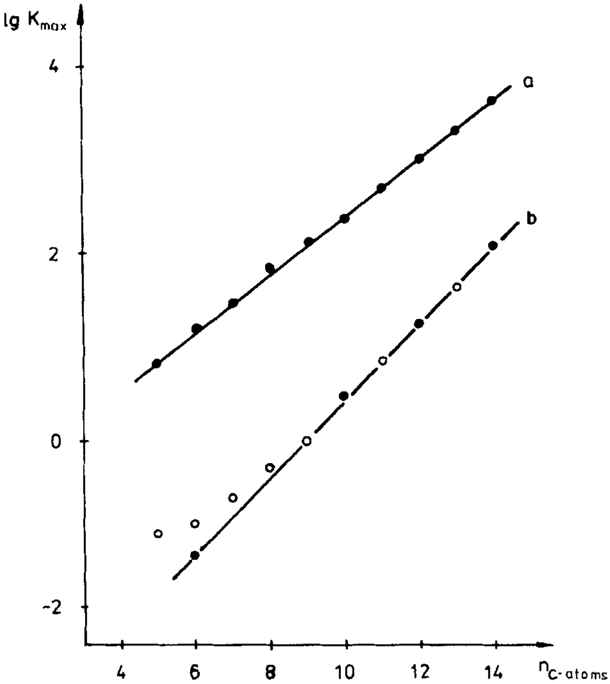

FIG. 4. Comparison of experimental and calculated maximum capacity ratio of *n*-paraffins. (a) Calculated by Eq. (1), (b) calculated by Eq. (2). (O) Experimental values, (●) calculated values.

Estimation of the Second Virial Coefficients

The correspondence of the curve maxima positions in Fig. 3 obtained experimentally and calculated is remarkably good between 1.5 and 2 MPa. This opens the simple possibility of estimating the second virial coefficient of the paraffins by means of the pressure p_{max} obtained experimentally by using an equation obtained by differentiating Eq. (1) and assuming $\Delta_{12} = 0$ (i.e., the second virial cross coefficient is the arithmetic average of the second virial coefficients of the pure components):

$$B_{22} = v_{02} - \frac{RT}{p_{max}} \quad (3)$$

In Fig. 5 the B_{22}/T diagram of *n*-tridecane based on Eq. (3) and our experimentally determined values of p_{max} are compared with theoretical values calculated by different approximation equations. Values obtained experimentally coincide well with the group of lower values. Taking into consideration that as a matter of experience the B_{22} values calculated theoretically are usually too high, supercritical fluid chromatography seems to be a useful method for the estimation of second virial coefficients despite the simple calculation procedure.

The difference between experimental and calculated values of p_{max} found for the higher paraffins is due to the simple arithmetic mixing rule, originally derived for similar molecules.

Group Separation

The pressure-programmed supercritical chromatogram of an industrial paraffin sample (VEB PCK Schwedt, DDR) including chain lengths C_{10} to C_{20} is shown in Fig. 6. The paraffin sample is injected into a molecular sieve 5A column under normal gas-chromatographic conditions. At a column temperature of 200°C (in practice it was necessary to use 200°C although 100°.C was adequate for rapid elution of eicosane at high pressure conditions to achieve a rapid elution of the isoparaffins at low pressure conditions) and a pressure of 0.5 MPa, the isoparaffin fraction of the whole chain-length range is quickly eluted as a compact peak. The completeness of elution has been proved by check measurements. Supercritical gas effluents were analyzed by temperature-programmed gas chromatography.

After increasing the pressure in one step from 0.5 to 10 MPa, the *n*-paraffins are eluted quickly.

After complete elution of the *n*-paraffins, the column is prepared for the next analysis by decreasing the pressure to 0.5 MPa by means of an expansion valve. The next run can be started after a stabilization time of 5 min.

Quantitative Analysis

The supercritical chromatogram shown in Fig. 6 provides the quantitative composition of the paraffin sample by means of the calibration curves shown in Fig. 7. The calibration curves are characterized by correlation coefficients of 0.99 and 0.975, respectively, and provide usable quantitative results.

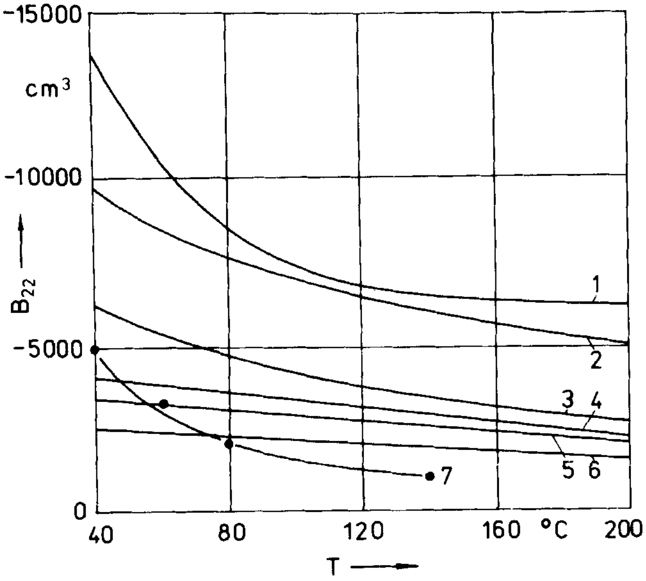

FIG. 5. Comparison of experimental and calculated second virial coefficients of *n*-tridecane.

(1) Pitzer and Curl:

$$B_{22} = \frac{RT_k}{p_k}\left[0.1445 - \frac{0.35}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} + \omega\left(0.073 + \frac{0.46}{T_r} - \frac{0.50}{T_r^2} - \frac{0.097}{T_r^3} - \frac{0.0073}{T_r^8}\right)\right]$$

(2) Wohl:

$$B_{22} = \frac{RT_k}{p_k}\left(0.197 - \frac{0.546}{T_r} - T_r\right)$$

(3) Berthelot:

$$B_{22} = \frac{RT_k}{p_k}\left(0.0686 - \frac{0.4116}{T_r}\right)$$

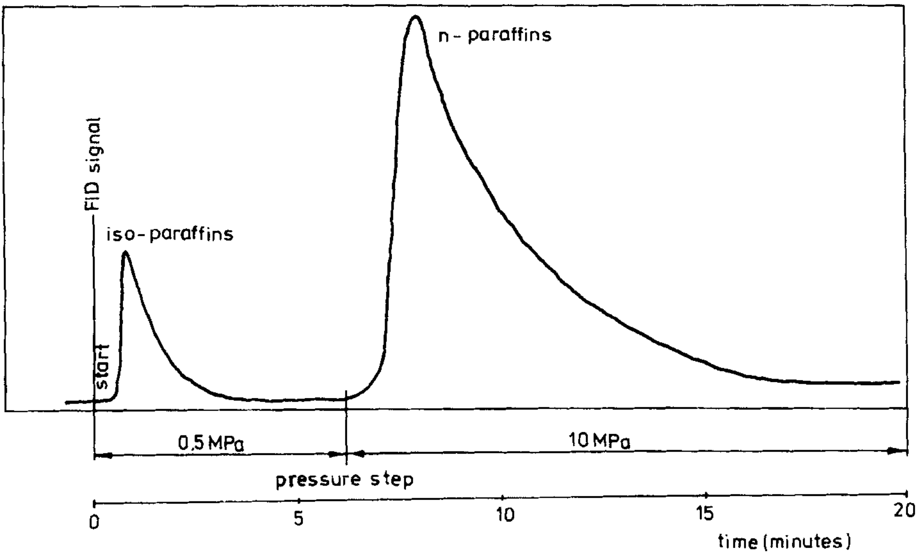

FIG. 6. Pressure programmed separation of an industrial C_{10}-C_{20} paraffin sample. Stationary phase, molecular sieve 5A; mobile phase, carbon dioxide; 60 L/h NPT (20°C, 760 torr); column temperature, 200°C; sample size, 3 μL.

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(4) Redlich:

$$B_{22} = \frac{RT_k}{p_k}\left(0.0867 - \frac{0.4278}{T_r}\right)$$

(5) Dieterici:

$$B_{22} = \frac{RT_k}{p_k}\left(0.1353 - \frac{0.5412}{T_r}\right)$$

(6) Van der Waals:

$$B_{22} = \frac{RT_k}{p_k}\left(0.125 - \frac{0.422}{T_r}\right)$$

(7) Experimental.

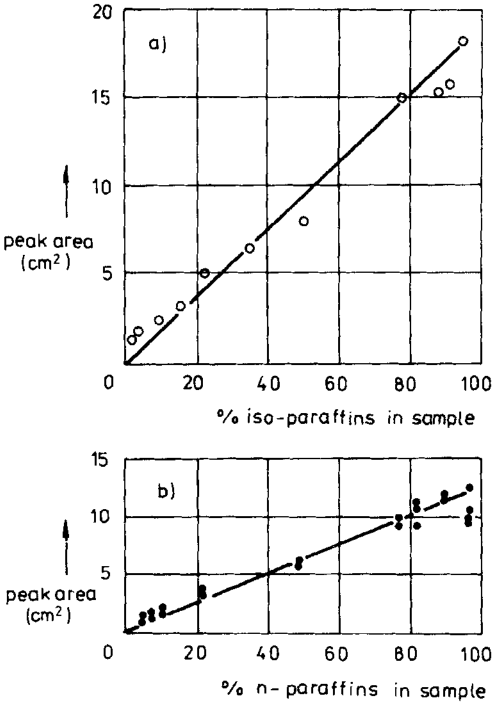

FIG. 7. Calibration curves for a C_{10}–C_{20} paraffin sample for an absolute quantity of total iso- and *n*-paraffins.

PREPARATIVE SCALE CHROMATOGRAPHY

Group Separation of *n*- and Isoparaffins

Separation and extraction processes at supercritical conditions have been increasingly discussed and technically applied during the past few years (*12*). Because it combines elements of distillation and supercritical extraction, Zosel termed this method "destraction" (*13*).

In the present work, supercritical chromatography has been applied to the preparative production of *n*-paraffins of chain length C_{10} to C_{20} from mineral oil distillates. The principle of supercritical fluid chromatography has been combined with pressure-programmed high pressure extraction for large-scale separation. The resulting procedure is a chromatographic two-step process with a low-pressure first step for the elution of the isoparaffins and a high-pressure second step for desorption of the *n*-paraffins from molecular sieve 5A by fluid carbon dioxide.

Apparatus

The apparatus for preparative high-pressure chromatography is presented in Fig. 8. Depending upon the applied pressure, the extraction medium CO_2 flows from the gas cylinder at ambient temperature in the gaseous or liquid state to the column section where it is preheated in a capillary coil. For work at low pressures (0.5–6 MPa), gaseous CO_2 is expanded to the required pressure by a pressure regulator.

The CO_2 grade is the same as in analytical experiments.

For working at high pressure (6–20 MPa), liquid CO_2 is compressed by a high-pressure membrane metering pump, model HM 1 (Lewa KG, Leonberg, BRD). The pump head is cooled to +10°C by means of a water jacket.

Pressure control is carried out in two steps. In the first step the CO_2 pressure is roughly controlled by manually changing the plunger stroke of the pump. Fine control is automatically carried out in the second step by means of a servocontrolled bypass valve M (in-house manufactured) which is controlled by a contact manometer CM. The components PC and PR are used for electronic pressure control (PC) and programming (PR) by a time-controlled electronic programmer.

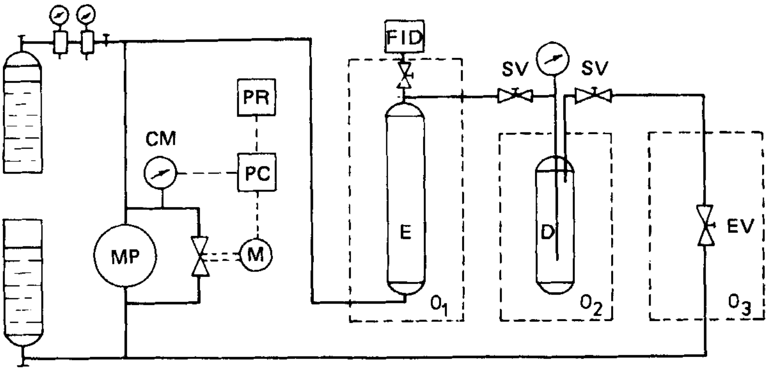

FIG. 8. Apparatus for preparative scale supercritical chromatography. MP, membrane metering pump; PR, pressure programmer; PC, pressure control; M, motor valve; E, extraction vessel; EV, expansion valve; O, oven; D, demixing vessel; SV, switching valve; CM, contact manometer.

The supercritical medium CO_2 is pumped through a 0.5-m long preheating capillary, i.d. 0.16 mm, into the extraction vessel E located in the oven of the gas chromatograph model GCHF 18.3/4. The volume of the extraction vessel is 50 mL (stainless steel cylinder, 2 cm i.d.). The carbon dioxide is pumped through the extraction vessel, demixing vessel (stainless steel cylinder, 2 cm i.d.), and expansion valve EV in a closed cycle.

The supercritical medium and the substance extracted form a homogeneous supercritical phase in the extraction vessel.

In the demixing vessel D the extract is deposited by expansion to 2 MPa and/or a temperature decrease to 50°C of the carrier gas.

The extract is collected in a glass vessel inserted in D and tared prior to installation.

Different demixing vessels can be switched into the extraction medium cycle by means of manually operated, in-house manufactured shut-off valves. All demixing vessels are located in the same thermostat and pressure controlled by the same valve.

The extraction process is monitored by means of an FID which indicates the full-time signal of the destraction effluent concentration with a split ratio of 1:100.

PROCEDURE AND RESULTS

Mineral oil distillate (4 g) containing *n*-paraffins of chain lengths C_{10}–C_{20} is distributed on 35 g molecular sieve 5A (particle size 0.16–0.215 mm) in the liquid state. The externally loaded molecular sieve is placed in the extraction vessel which is switched to the CO_2 cycle. The run begins by starting the CO_2 flow. In the first separation step, 1.7 g isoparaffins (including small amounts of olefins, aromatics, and cyclic paraffins) are desorbed as a group selectively from other mineral oil components using normal gas chromatographic conditions ($p = 0.5$ MPa, $T = 200°C$, $V = 40$ L/h).

After the complete elution of this so-called isofraction, shown by the FID signal, a second demixing vessel is switched in-line, the column pressure is increased suddenly to 10 MPa, and the elution of the *n*-paraffins starts immediately. The *n*-paraffin elution is completed in 20 min. The 4-g sample contained 1.65 g *n*-paraffins.

After cooling and loading a new molecular sieve, the next separation cycle can be started.

The molecular sieve can be used for some 10 cycles without effecting the reproducibility of separation and without visible residue on the molecular sieve.

The difference of 0.65 g in the sample left during the procedure is due to loss at collection and by combustion by the FID.

The cycle time can be decreased drastically by internal loading: for example, loading the hot molecular sieve at a pressure of 0.5 MPa by means of a metering pump. Further, the amount per run can be increased by both increasing the scale and using a system of shunted columns.

The result of preparative scale separation was demonstrated by analytical gas chromatography. Figure 9 shows a chromatogram of unextracted mineral oil distillate. The unseparated peaks are isoparaffins, aromatics, olefins, and cyclic paraffins present in the distillate along with the *n*-paraffins separated. Figure 10 shows the composition of the isofraction obtained by the separation procedure. This chromatogram corresponds to the unresolved species discussed in Fig. 9. The analytical chromatogram of the *n*-paraffin fraction is shown in Fig. 11. The purity of

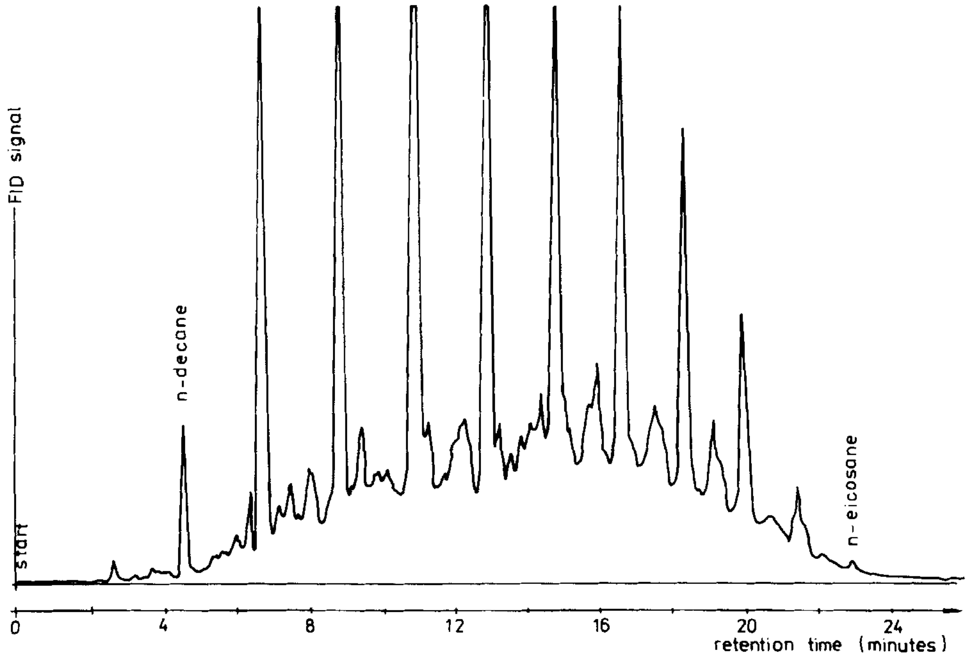

FIG. 9. Analytical chromatogram of an industrial *n*- and isoparaffin sample (content of *n*-paraffins = 50%). Gas chromatograph HP 5830 A, column 10% W 98 on chromosorb, 2 m × $\frac{1}{8}$"; column temperature, 50–300°C, 2°C/min; carrier gas, nitrogen, 30 mL/min; flame ionization detector; sample size, 1 μL.

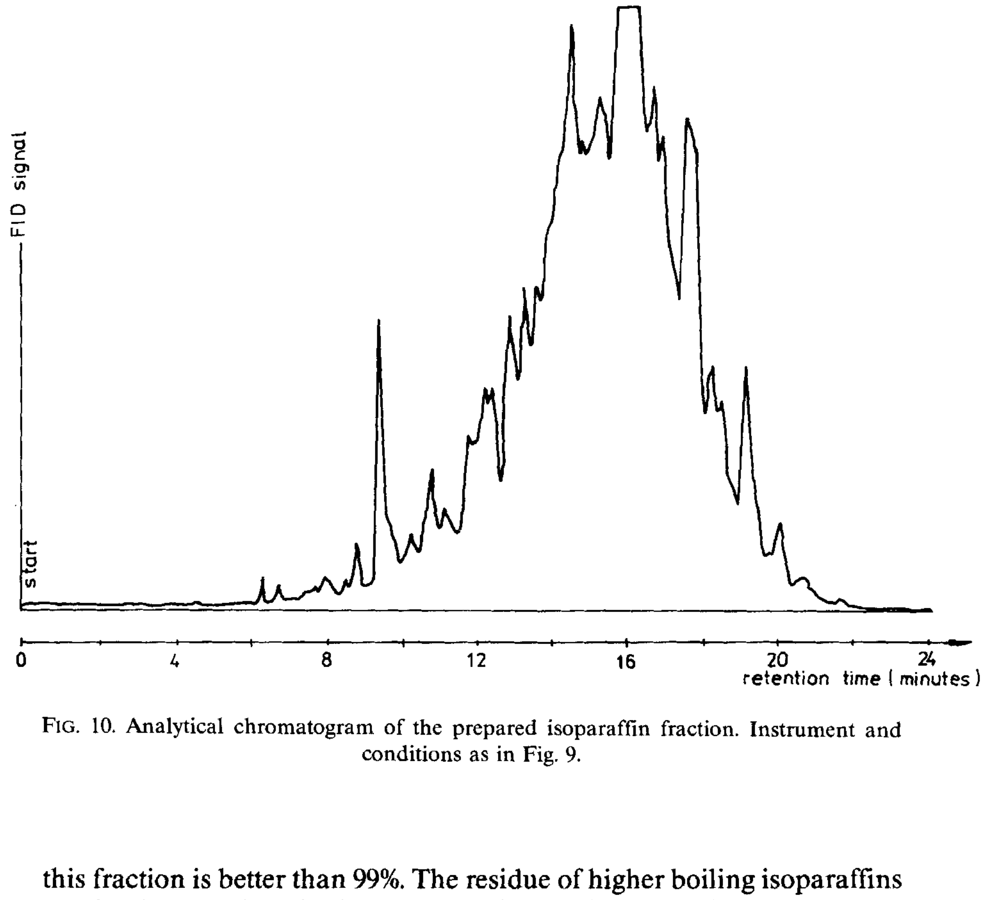

FIG. 10. Analytical chromatogram of the prepared isoparaffin fraction. Instrument and conditions as in Fig. 9.

this fraction is better than 99%. The residue of higher boiling isoparaffins can be decreased by further optimization of the separation conditions.

CONCLUSIONS

The elution of *n*-paraffins C_{10}-C_{20} from molecular sieve 5A is possible at mild thermal conditions using CO_2 at supercritical conditions.

Based on this effect, a procedure has been developed to separate *n*- and isoparaffin groups on both analytical and preparative scales.

Besides the results of group selectivity and quantitation, analytical application of supercritical chromatography permits estimation of second virial coefficients of the paraffins with good approximation to values obtained by other methods. However, the theoretical basis must be improved to obtain better physicochemical constants.

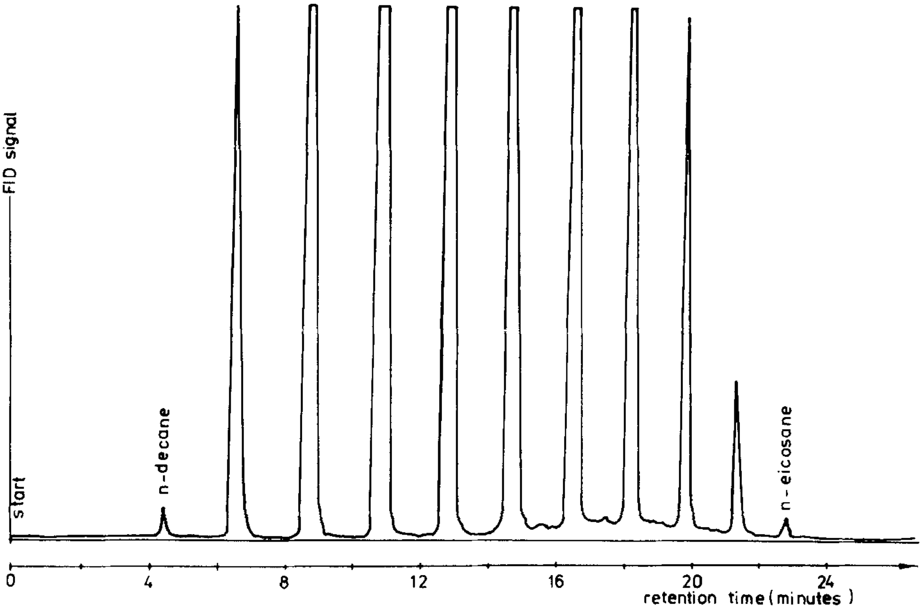

FIG. 11. Analytical chromatogram of the prepared *n*-paraffin fraction. Instrument and conditions as in Fig. 9.

Consideration of the influence of the stationary phase on the partition coefficient should make a better characterization of the molecular sieve effect within the supercritical system possible.

Industrial samples of *n*- and isoparaffin groups can be selectively separated from a mineral oil on a preparative scale. It appears possible to decrease the cycle time mainly by loading the molecular sieve with the mineral oil sample at the first step of the working conditions by using a metering pump and then by automatization of further steps of the process.

Further optimization of the separation process parameters with regard to energy and time costs and to the purity of the fractions should be pursued.

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