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High-Pressure Gas Chromatography and Chromatography with Supercritical Fluids. I. The Effect of Pressure on Partition Coefficients in Gas-Liquid Chromatography with Carbon Dioxide as a Carrier Gas

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High-Pressure Gas Chromatography and Chromatography with Supercritical Fluids. I. The Effect of Pressure on Partition Coefficients in Gas-Liquid Chromatography with Carbon Dioxide as a Carrier Gas

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Summary

Gas-chromatographic experiments with CO_2 as a carrier gas, conducted at temperatures of 30 to 40°C and pressures up to 80 atm, showed a pronounced drop of the partition coefficient with increasing pressure. This effect, which can be interpreted as a raise in solute volatility, is proved to be mainly due to nonideality in the gas phase.

The gain in volatility (by a factor of 10 or more) permits gas-chromatographic separations to be carried out at lower temperatures than usual. As partition coefficients were found to drop very fast near the critical point of the carrier gas, operation at pressures well above this point may open up the possibility of handling compounds too heavy for ordinary gas-chromatographic practice.

Interesting possibilities of class separation can be deduced from the study of the pressure effect in homologous series. Some potential non-analytical applications of high-pressure gas chromatography are discussed.

INTRODUCTION

An important limitation of gas chromatography is the requirement that substances to be separated have to be reasonably volatile. Lack of volatility is reflected in excessively long elution times and solute concentrations in the effluent gas which are too low to be detectable.

Adaptation of the chromatographic system to lower the volatility requirements may include using more sensitive detectors and reducing the amounts of stationary phase to the minimum consistent with the separation. Highly sensitive ionization detectors, low-loaded packed columns, and open-bore capillary columns have indeed shifted the limit of applicability to heavier compounds.

An obvious means of increasing solute volatility is to raise the working temperature. However, a limit is set by the heat stability of the solute and the stationary phase. Limitation due to volatility of the latter can, in principle, be overcome by using products of higher molecular weight.

Another possibility of increasing solute volatility is the use of molecular interactions between solute and carrier gas, viz., by working with a nonideal gas at elevated pressures. It is well known, for instance, that solids exhibit greater vapor pressures when present in high-pressure gases, and particularly in supercritical fluids. As no systematic investigation has yet been undertaken to exploit this phenomenon in GLC, we have studied the influence of carrier gas pressure on equilibrium constants.

PREVIOUS WORK ON THE ROLE OF THE CARRIER GAS IN GLC

In the idealized theoretical treatment of gas chromatography the transporting medium is regarded as an ideal gas, vapor-liquid equilibria being treated as pseudobinary. Hence, for a given solute and stationary phase, the partition coefficient is only dependent upon temperature.

To increase precision, corrections for carrier gas imperfectness have been applied by a few workers who determined activity coefficients by means of a gas-chromatographic technique (*1–4*). Goldup et al. (*5,6*) studied more systematically the nonperfect behavior of the carrier gas in capillary GLC; slight variations in retention times were attributed to imperfection of the gas phase. More recently, Luckhurst (*7*) studied the effect of nonideality of the gas phase in frontal analysis, and Martire and Locke (*8*) derived an equation for obtaining the mean column pressure in gas-chromatographic columns for slightly imperfect carrier gases.

After completion of the present study, a few more papers have appeared which deal with nonideality of the carrier gas. Sewell and Stock (*26*) investigated the effect of carrier gas on gas-liquid partition. Using a quartz-spring balance, they made some measurements by a nonchromatographic procedure in the pressure range up to 80 cm Hg. The effect of gas solubility in the liquid is neglected.

Locke (27) considered the combined effects of nonideality of the gas and adsorption of carrier gas molecules in gas-solid chromatography. The latter is taken to diminish the surface area available to the solute. Assuming a linear or a Langmuir adsorption isotherm, different equations were derived. No experimental data are presented, however.

Everett (28) made a thorough analysis of gas imperfection in GLC measurements and derived equations that relate the net retention volume with the activity coefficient at infinite dilution in the stationary liquid for a case where the gas phase deviates from ideality and where an appreciable pressure drop occurs across the column. He applied his theory to some of the above-mentioned experiments by Desty et al. (6), as well as to a few unpublished data of Windsor which pertain to similar experiments. Without considering the possible effect of the solubility of carrier gas in the liquid, Everett suggests that GLC measurements may be used for determining second virial coefficients.

In the systems studied by the authors mentioned above, conditions of the gas phase were typical of or at most only slightly different from normal GLC. Under these conditions, deviation from perfect-gas behavior is slight and results in variations in partition coefficients of a few per cent at most. To quote Locke (27): "Analytically, most systems behave ideally (in a thermodynamic sense) for all practical purposes."

Our efforts have been directed to the investigation of systems deviating more widely from perfect-gas behavior.

CHOICE OF SYSTEMS STUDIED

Among the gases commonly used in GLC (viz., He, H_2, A, N_2, and CO_2) carbon dioxide deviates most from a perfect gas. As, moreover, its critical point is rather favorably situated from an experimental point of view (31.1°C, 73 atm), we have employed it throughout the present investigation.

Squalane and glycerol were chosen as examples of apolar and polar stationary liquids, respectively. Moreover, these liquids differ markedly with regard to their solvent power for CO_2, as will be shown later.

The solutes chosen belong to different classes (saturated hydrocarbons, olefins, aromatics, alcohols, ketones, and halogenated compounds). In view of the temperature range studied (30 to 40°C) components of relatively low molecular weight were examined.

THEORETICAL

Effect of Gas Pressure on Partition Coefficients

The partition (distribution) coefficient k in GLC is defined as

$$k = \frac{\text{amount of solute per unit volume of stationary liquid phase}}{\text{amount of solute per unit volume of gas phase}} \qquad (1)$$

A change in carrier gas pressure may alter k in three ways:

1. Interaction between carrier gas molecules and solute molecules.
2. Effect of "mechanical" pressure on the stationary liquid.
3. Solution of carrier gas into the stationary liquid, thereby changing its nature.

If the gas phase deviates from a perfect gas—i.e., intermolecular forces are not negligible—the extent to which these forces affect k is dependent on the average distances between the molecules, hence on pressure. A measure of the departure from perfect-gas behavior (for slightly imperfect gases) is the second virial coefficient B, which for a binary mixture is a quadratic function of composition

$$B_m = (1 - y)^2 B_{1,1} + 2y(1 - y)B_{1,2} + y^2 B_{2,2} \qquad (2)$$

where y is the mole fraction of component 2. $B_{1,1}$ and $B_{2,2}$ (the coefficients of the two pure gases) are functions solely of the temperature and the forces between 1,1 and 2,2 pairs of molecules, respectively.

$B_{1,2}$ is an identical function of the 1,2-forces. The interaction between carrier gas and solute may, therefore, be described by the second virial cross coefficient $B_{1,2}$.

The exertion of mechanical pressure on the liquid generally causes the equilibrium vapor pressure of the solute to increase; its change depends on the partial molar volume of solute in the liquid. As to carrier gas solubility, the varying composition of the stationary liquid caused by changes in carrier gas pressure may affect the activity coefficient of the dissolved solute. Unfortunately, it is not possible to derive a simple formula which permits calculation of this effect. A thermodynamic approach is possible for the effects mentioned under 1 and 2.

For the nonideal gas phase the relationship between volume (V_g), number of moles (n_g), pressure (P), and temperature (T) can be written

$$\frac{V_g}{n_g}=\frac{RT}{P}+B_m=\frac{RT}{P}\left(1+\frac{P}{RT}B_m\right) \tag{3}$$

so that

$$\ln\left(\frac{V_g}{n_g}\right)=\ln RT-\ln P+\ln\left(1+\frac{P}{RT}B_m\right) \tag{4}$$

which, for small deviations from ideality $[(P/RT)B_m \ll 1]$, is simplified to

$$\ln\left(\frac{V_g}{n_g}\right)=\ln RT-\ln P+\frac{P}{RT}B_m \tag{5}$$

Because in gas chromatography solute concentrations are generally very small (y approaches zero), B_m approaches $B_{1,1}$ [see Eq. (2)]. Equation (5) becomes

$$\ln\left(\frac{V_g}{n_g}\right)=\ln RT-\ln P+\frac{P}{RT}B_{1,1} \tag{6}$$

As $B_{1,1}$ is a temperature function only, differentiation of (6) yields

$$\frac{d\ln(V_g/n_g)}{dP}=-\frac{1}{P}+\frac{B_{1,1}}{RT} \tag{7}$$

The chemical potential $(\mu_2)_{\text{gas}}$ of the solute in the gas phase can be written [see (*24*), Eq. 5.13.3, and (*25*), Eq. 8.07.3)

$$(\mu_2)_{\text{gas}}=\mu_2^+ + RT\ln y+RT\ln\frac{P}{P^+} + P[B_{2,2}+(1-y)^2(2B_{1,2}-B_{1,1}-B_{2,2})] \tag{8}$$

where P^+ is a standard pressure and μ_2^+ is the standard chemical potential. As $y \ll 1$, Eq. (8) reduces to

$$(\mu_2)_{\text{gas}}=\mu_2^+ + RT\ln y+RT\ln\frac{P}{P^+}+P(2B_{1,2}-B_{11}) \tag{9}$$

The pressure dependence of $(\mu_2)_{\text{gas}}$ at constant T can (taking into consideration that μ_2^+, $B_{1,2}$, and $B_{1,1}$ are functions of temperature only) be written

$$\frac{\partial(\mu_2)_{\text{gas}}}{\partial P} = \frac{RT}{P} + RT\frac{d(\ln y)}{dP} + (2B_{1,2} - B_{1,1}) \tag{10}$$

Considering the liquid phase as a binary mixture of stationary solvent and solute, the pressure dependence of the chemical potential of the solute at constant x (molar fraction of solute in liquid phase) and T is given by [see (*24*), Eq. 6.15.2]

$$\frac{\partial(\mu_2)_{\text{liq}}}{\partial P} = V_2 \tag{11}$$

where V_2 is the partial molar volume of solute in the liquid.

If we consider the vapor-liquid equilibrium at constant T and constant liquid composition* but at varying pressure, the equilibrium condition may be written

$$\frac{\partial(\mu_2)_{\text{gas}}}{\partial P} = \frac{\partial(\mu_2)_{\text{liq}}}{\partial P} \qquad (x, T \text{ constant}) \tag{12}$$

or, from combination with Eqs. (10) and (11),

$$\frac{d(\ln y)}{dP} = -\frac{1}{P} - \frac{2B_{1,2} - B_{1,1} - V_2}{RT} \tag{13}$$

The partition coefficient k can be written

$$k = \frac{x}{y}\frac{n_l}{V_l}\frac{V_g}{n_g} \tag{14}$$

or

$$\ln k = \ln x - \ln y + \ln\frac{n_l}{V_l} + \ln\frac{V_g}{n_g} \tag{15}$$

where n_l and n_g are the total number of moles contained in a liquid volume V_l and gas volume V_g.

At constant x, and neglecting the compressibility of the liquid (i.e., taking V_l independent of pressure), we obtain from Eq. (15),

$$\frac{d(\ln k)}{dP} = -\frac{d(\ln y)}{dP} + \frac{d[\ln (V_g/n_g)]}{dP} \tag{16}$$

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* This is equivalent to considering the equilibrium with an infinite amount of liquid phase.

Combining Eqs. (7), (13), and (16), we obtain

$$\frac{d(\ln k)}{dP} = \frac{2B_{1,2} - V_2}{RT} \tag{17}$$

Again neglecting the liquid compressibility (taking the partial molar volume of solute in liquid as pressure-independent), we obtain by integrating Eq. (17),

$$\ln k_P = \ln k_{P_0} + \frac{P - P_0}{RT} (2B_{1,2} - V_2) \tag{18}$$

where P_0 is an arbitrarily chosen reference pressure, e.g., 1 atm, or such a low pressure that the gas phase may be regarded as perfect. In the latter case k_{P_0} becomes a constant which for a given solute and stationary solvent is a function of temperature only, regardless of the nature of the carrier gas.

Principle of Corresponding States

In the absence of experimental data on $B_{1,2}$ values, an estimate of the interaction coefficients is possible by assuming that the binary mixtures involved obey the principle of corresponding states. According to this principle (9), the dependence of the second virial coefficient B of a substance on temperature has the form

$$\frac{B}{V^*} = \varphi \left(\frac{T}{T^*}\right) \tag{19}$$

where φ is a universal function valid for all substances conforming to this principle. V^* and T^* are a characteristic volume and temperature for which the critical molar volume and the critical temperature are usually adopted.

For a binary mixture conforming to this principle it can be shown (9) that the interaction coefficient obeys an analogous expression

$$\frac{B_{1,2}}{V^*_{1,2}} = \varphi \left(\frac{T}{T^*_{1,2}}\right) \tag{20}$$

where φ is the same function as before. To find $V^*_{1,2}$ and $T^*_{1,2}$ from the critical constants of the components, averaging rules are required. If the molecules behave as spheres and if the most important contribution to the interaction energy is due to London dispersion forces, these rules are

$$r^*_{1,2} = \tfrac{1}{2}(r^*_{1,1} + r^*_{2,2}) \tag{21}$$

and

$$\epsilon^*_{1,2} = (\epsilon^*_{1,1}\epsilon^*_{2,2})^{1/2} \tag{22}$$

where r^* is a characteristic dimension pertaining to the molecules (e.g., the collision diameter) and ϵ^* is a characteristic interaction energy (depth of the potential well). Subscripts 1,1, 2,2, and 1,2 denote pairs of molecules of type 1, type 2, and a pair of different molecules 1 and 2, respectively.

The above-mentioned rules can also be formulated as

$$(V^*_{1,2})^{1/3} = \tfrac{1}{2}(V^*_{1,1})^{1/3} + \tfrac{1}{2}(V^*_{2,2})^{1/3} \tag{23}$$

$$T^*_{1,2} = (T^*_{1,1}T^*_{2,2})^{1/2} \tag{24}$$

With the aid of these equations $B_{1,2}$ can be calculated from the critical constants of the pure components if the function φ from Eq. (20) is known. Several functions have been proposed in the literature (9), two of which have been used in our subsequent calculations:

$$\frac{B_{1,2}}{V^*_{1,2}} = 0.438 - 0.881\left(\frac{T^*_{1,2}}{T}\right) - 0.757\left(\frac{T^*_{1,2}}{T}\right)^2 \tag{25}$$

$$\frac{B_{1,2}}{V^*_{1,2}} = 0.461 - 1.158\,\frac{T^*_{1,2}}{T} - 0.503\left(\frac{T^*_{1,2}}{T}\right)^3 \tag{26}$$

EXPERIMENTAL

Quantity Measured

The quantity measured, k' (a modified partition coefficient, often called the capacity ratio), is related to the true partition coefficient k by

$$k' = k\,\frac{V_L}{V_G} \tag{27}$$

V_G and V_L being the volume of the gas phase and the liquid phase in the column. The elution volume V_R of a solute can be written

$$V_R = V_G + kV_L = (1 + k')V_G \tag{28}$$

At constant flow rate through the column, elution volumes are proportional to elution times; hence

$$t_R = (1 + k')t_G \tag{29}$$

k' is thus found by measurement of the elution time of a solute (t_R) and the holdup time of an inert gas (t_G).

Apparatus and Technique

The apparatus used, suitable for working pressures up to 80 atm, is shown diagrammatically in Fig. 1. Carrier gas is obtained from a standard 13.5-liter cylinder containing commercial, pure-grade CO_2. This cylinder (1) is immersed in a 200-liter water bath (2), which can be kept either at 0°C (ice/water) or at a constant temperature above room temperature. For the latter purpose, the bath

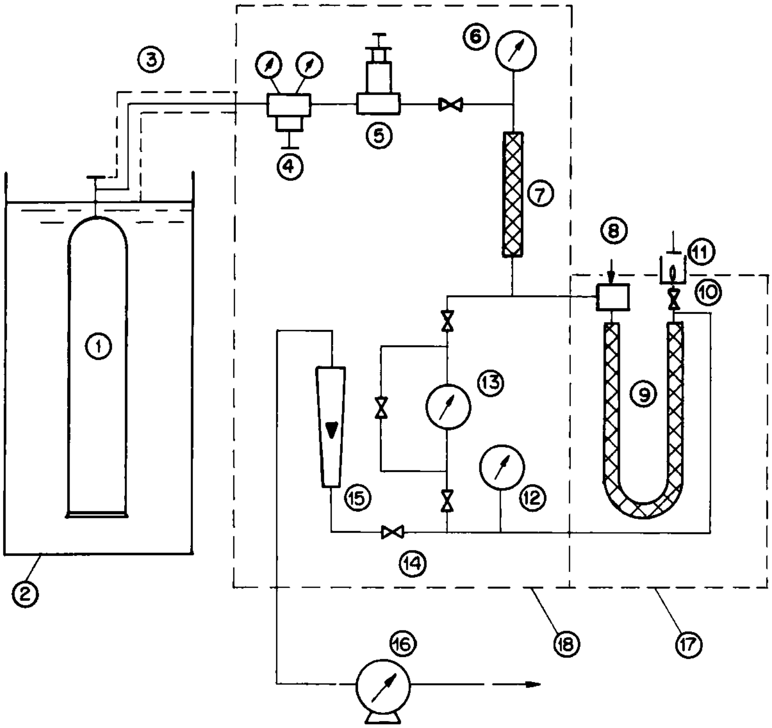

FIG. 1. Flow diagram of high-pressure gas-chromatographic apparatus (for explanation of figures see the text).

is provided with electric heating coils, contact thermometer, and a stirrer.

The cylinder pressure can be reduced by a high-pressure reducing valve (4), suitable for outlet pressures up to 50 kg/cm^2, and a precision low-pressure reducing valve (5) (Negretti and Zambra Ltd., suitable for outlet pressure up to approx. 5 kg/cm^2). Pressure is measured to the nearest 0.1 kg/cm^2 by means of a precision Bourdon gauge (6) and reported as average column pressure (the maximum pressure drop across the column was 0.5 kg/cm^2). At working pressures above 5 kg/cm^2, the low-pressure reducing valve is omitted. For pressures above 50 kg/cm^2, valve (4) is also omitted and the water bath temperature is adjusted to give the desired pressure (determined by vapor/liquid equilibrium). For pressures above the critical value (>73 atm), the temperature is also kept above the critical value (>31°C). In the latter case the cylinder charge is adjusted beforehand to give the desired pressure, care being taken that the cylinder does not become full of liquid during the heating-up stage.

To avoid recondensation of CO_2 at higher pressures, all high-pressure parts are kept in an air thermostat (18), a liquid thermostat (17), or they are heat-traced (3). Temperatures of air and liquid thermostats are constant to about 0.1 and 0.05°C, respectively.

To compensate for any evaporation losses in the column, the carrier gas is presaturated by passing it through a short column (7), containing exactly the same filling as the chromatographic column proper. The measurements are repeated occasionally to ensure that no losses of stationary liquid has occurred in the main column. Sample is injected by means of a pneumatic injector (8), shown in Fig. 2 (sample volumn 15 μl; suitable for pressures up to 100 kg/cm^2).

A conventional coiled GLC column (9) (1 m × 6 mm ID) is immersed in a liquid thermostat (17). Column filling consists of 30 parts (wt) of stationary liquid on 100 parts (wt) of support (Sil-O-Cel C 22 firebrick, 50/70 mesh). From the column effluent, a bleed stream (approx. 2 liters/hr at atmospheric pressure) is fed to the flame ionization detector (11). This bleed stream is adjusted by restriction valve (10); the pressure is reduced to atmospheric. Special care has been taken to ensure a minimum dead volume (about 20 μl) between the takeoff point of the main stream and the point where expansion takes place with a view to reducing holdup time.

Column outlet pressure is also measured by a precision Bourdon gauge (12). The pressure drop across the column can be accurately measured by means of a differential manometer (13) (0 to 500 cm H_2O, Barton Europa N.V.).

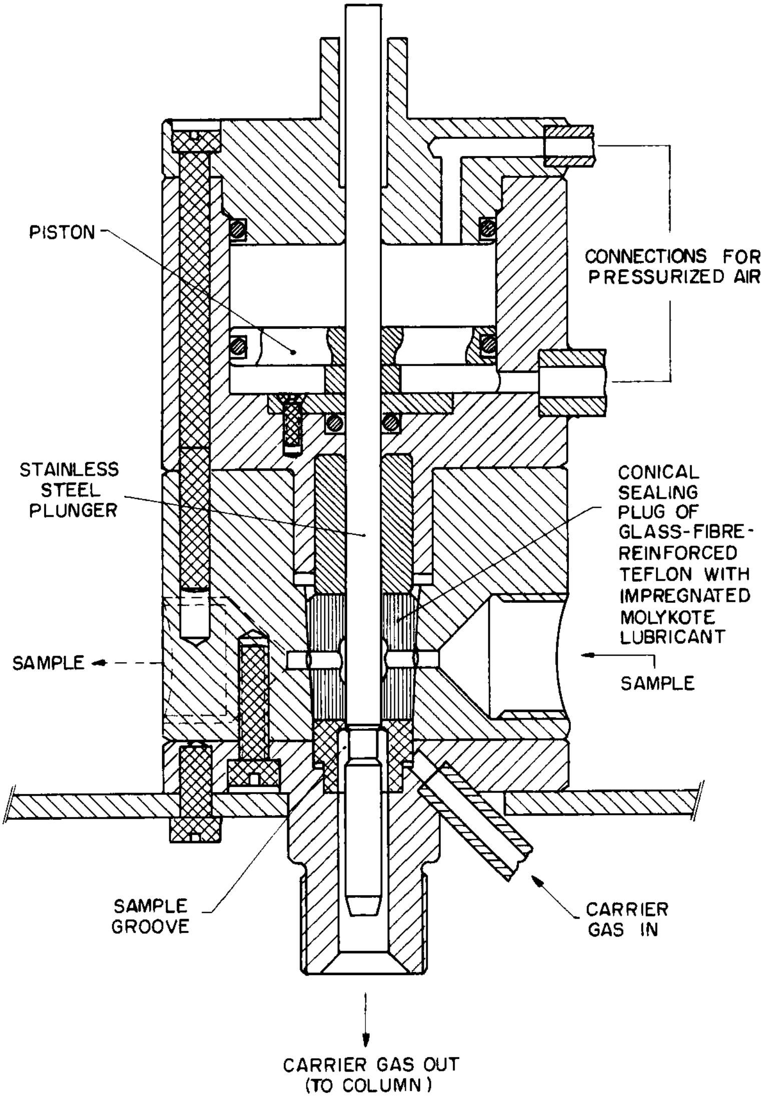

FIG. 2. Pneumatic sample injection device for pressures up to 100 kg/cm^2.

The main effluent stream is expanded via needle valve (14) (which serves to adjust the flow and maintain column pressure) and led to a rotameter (15). The quantity of CO_2 passed through in a certain time interval can also be determined by means of a wet-test meter (16) having a capacity of 3 liters per revolution.

The flame ionization detector is of conventional design. Hydrogen and air required to sustain the flame are purified and fed to the detector in the usual way. The detector signal is displayed on a potentiometric recorder via an impedance converter.

The detection principle applied makes small sample sizes possible (approx. 15 μl of gas); hence partition coefficients may be regarded as those for infinite dilution. However, as the detector does not respond to inorganic gases, the elution time t_G could not be determined on a truly inert gas such as He. We used methane instead, applying a correction for the finite solubility of this gas in the liquid. This correction (maximum 10%) is determined by comparing the retention times of He and CH_4 for the particular column in a conventional GLC apparatus, using a katharometer as a detector. The requisite correction was assumed to decrease linearly with increasing pressure, the value zero being reached for a pressure of 80 atm. The possible error due to this assumption is believed to be less than 2%.

The exact moment of injection was marked on the recorder chart by momentarily short-circuiting the recorder input by means of a microswitch. Recorder speed (up to 480 inches/hr) was adjusted to give accurately measurable distances between the peaks on the chart.

Each measurement of k' was carried out at a series of carrier gas velocities, ranging from about 0.2 to 10 cm/sec. Except for some experiments in the low-velocity region, k' proved to be virtually independent of flow rate. The deviations in the low-velocity regions may perhaps be attributed to changes of flow rate occurring in the long-duration experiments. These k' values (being higher by up to about 10%) were omitted.

Measurement of Carbon Dioxide Solubility

Two methods have been used, viz., a gas volumetric method for squalane having a high solvent power for CO_2, and a titrimetric method for glycerol which has a low one. In both methods the desired equilibrium conditions were established in a small stainless-steel cylinder, from which a sample of the liquid phase could be withdrawn for analysis. The usual precautions were taken to ensure representative sampling.

In the gas volumetric method the volume of gas which disengaged from a known weight of liquid was measured in a gas burette.

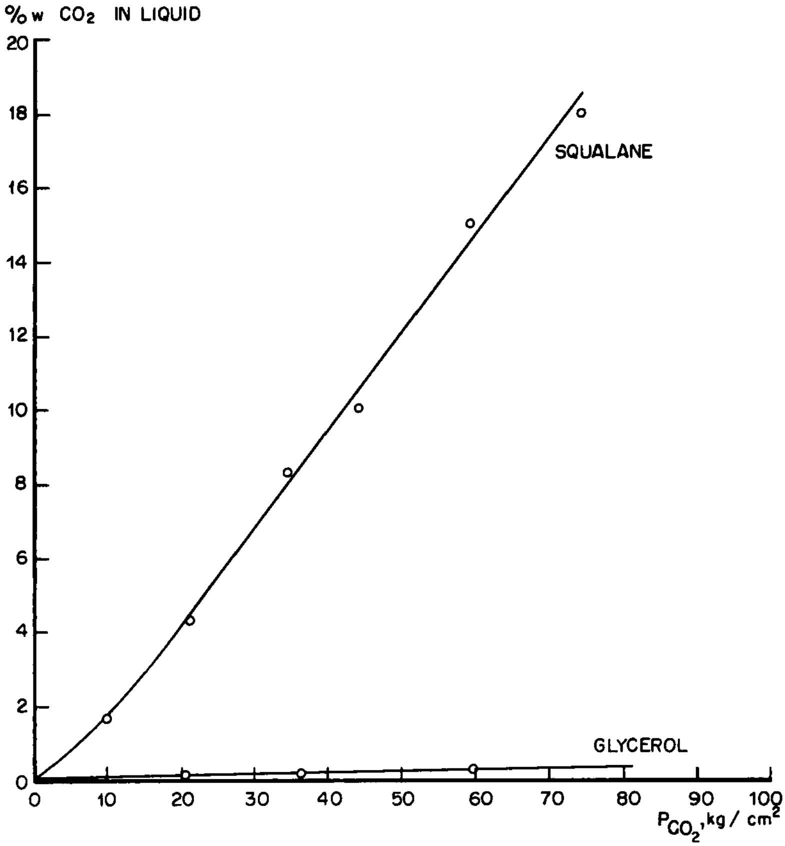

FIG. 3. Solubility of CO_2 in stationary phases. $T = 40°C$.

In the titrimetric method carbon dioxide was titrated in the liquid sample with 0.02 *N* sodium methanolate in anhydrous pyridine as titrant (thymol blue indicator). Care was taken to prevent escape of carbon dioxide to the atmosphere and contamination with atmospheric CO_2 during sampling and titration.

RESULTS

The results of k' measurements for propane, n-butane, n-pentane, 1,3-butadiene, benzene, methanol, ethanol, acetone, n-propyl chloride, and 1,1-dichloroethane are shown graphically in Figs. 4 to 9. Results of solubility measurements are given in Fig. 3.

DISCUSSION OF RESULTS

Effect of Pressure on k'

The effect is quite appreciable; with increasing pressure, k' drops. This means a quicker elution and may be regarded as an

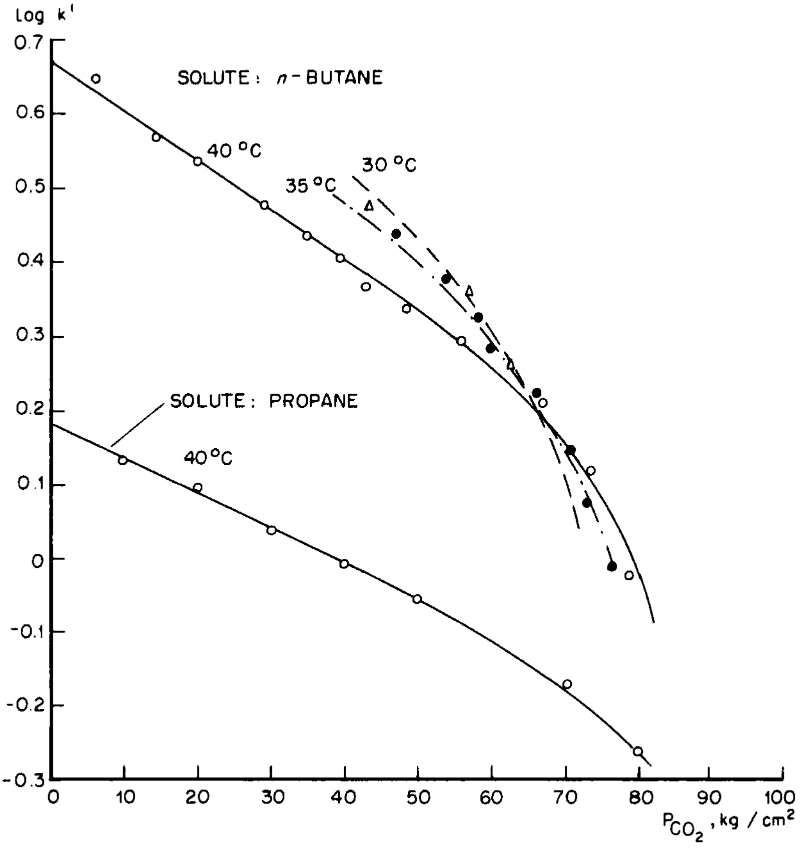

FIG. 4. Effect of CO_2 pressure on the partition coefficients of propane and n-butane on a squalane column.

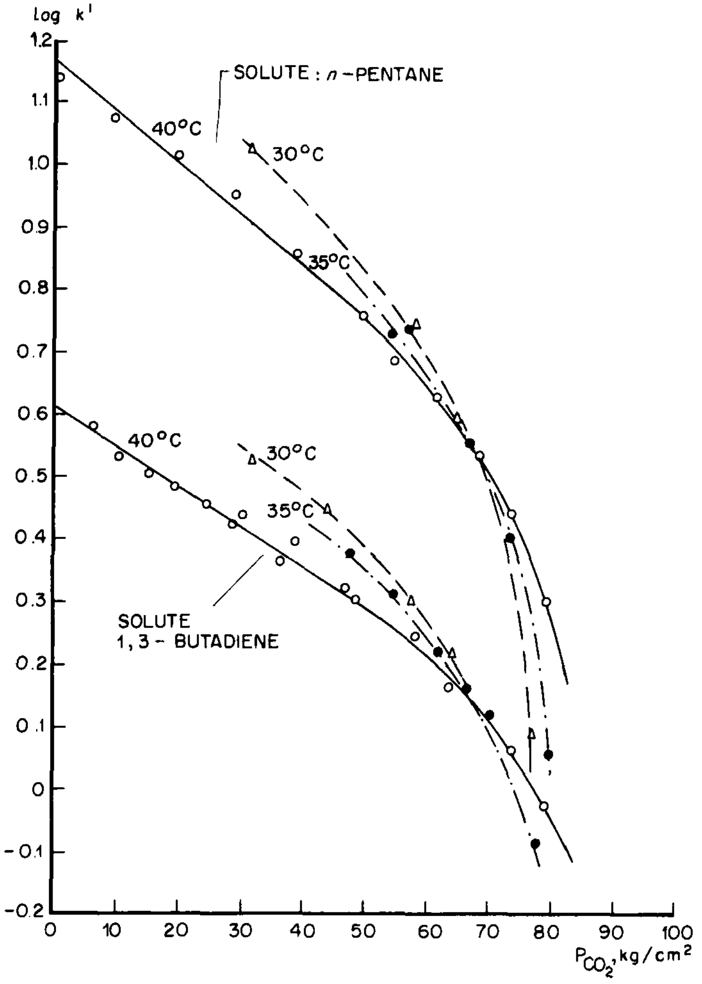

FIG. 5. Effect of CO_2 pressure on the partition coefficients of *n*-pentane and 1,3-butadiene on a squalane column.

enhancement of volatility of the solute. As we go from atmospheric pressure to 80 atm, k' may change by more than a factor of 10 (see Fig. 6). The effect is especially marked with pressures near the critical value for the carrier gas (73 atm).

From Eq. (18) we find for the dependence of k' on pressure

$$\log k'_P = \log k'_{P_0} + \frac{P - P_0}{2.303RT} (2B_{1,2} - V_2) \qquad (30)$$

As will be seen from Figs. 4 to 9, where the logarithm of k' is plotted against column pressure, the experimental results can be represented by a straight line up to about 50 atm, in accordance with this equation. For higher pressures, however, a deviation from the linear relationship is observed, k' decreasing more rap-

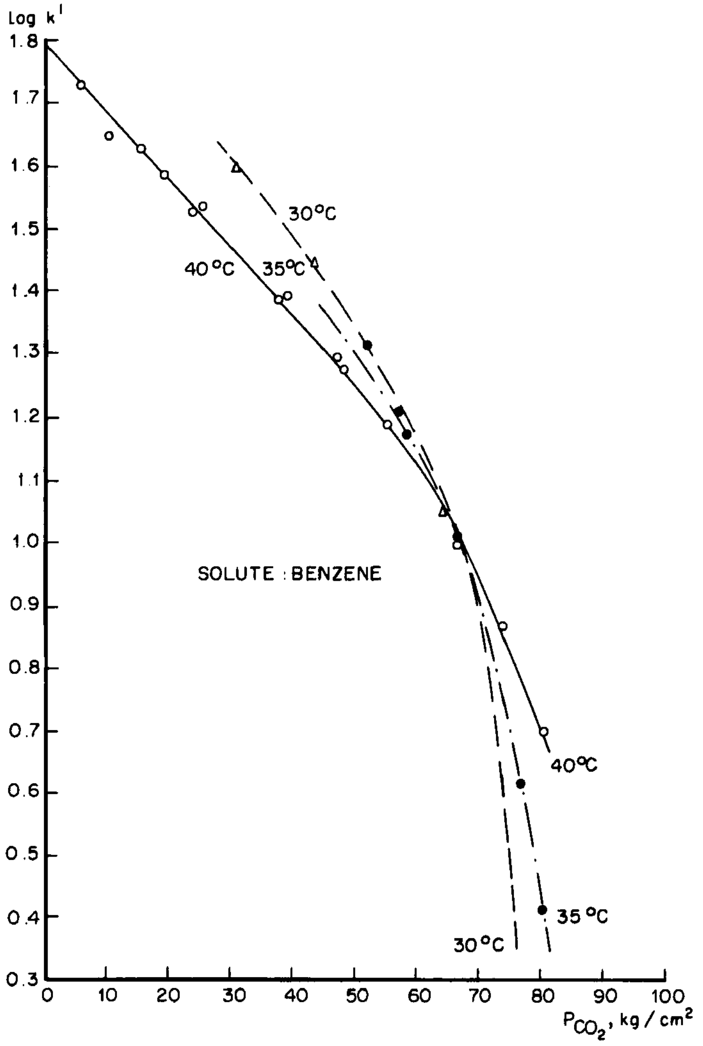

FIG. 6. Effect of CO_2 pressure on the partition coefficient of benzene on a squalane column.

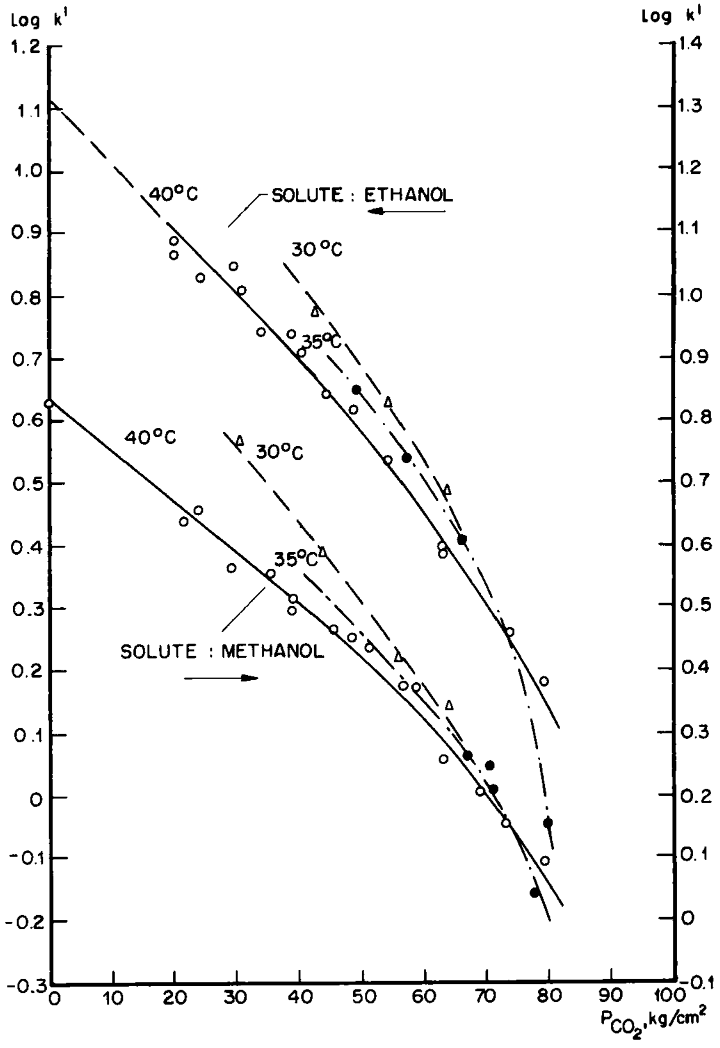

FIG. 7. Effect of CO_2 pressure on the partition coefficients of ethanol and methanol on a squalane column.

idly with increasing pressure. Obviously, virial coefficients of higher order are required to describe adequately the deviations from ideality in this region.

Although the initial part of the log *k'*-*P* plots conforms to F

(30), it may be questioned whether the observed effects are not the result of carbon dioxide dissolving in the liquid. Especially with squalane, CO_2 solubility can hardly be ignored (see Fig. 3). With glycerol, however, the solubility of CO_2 is quite small.

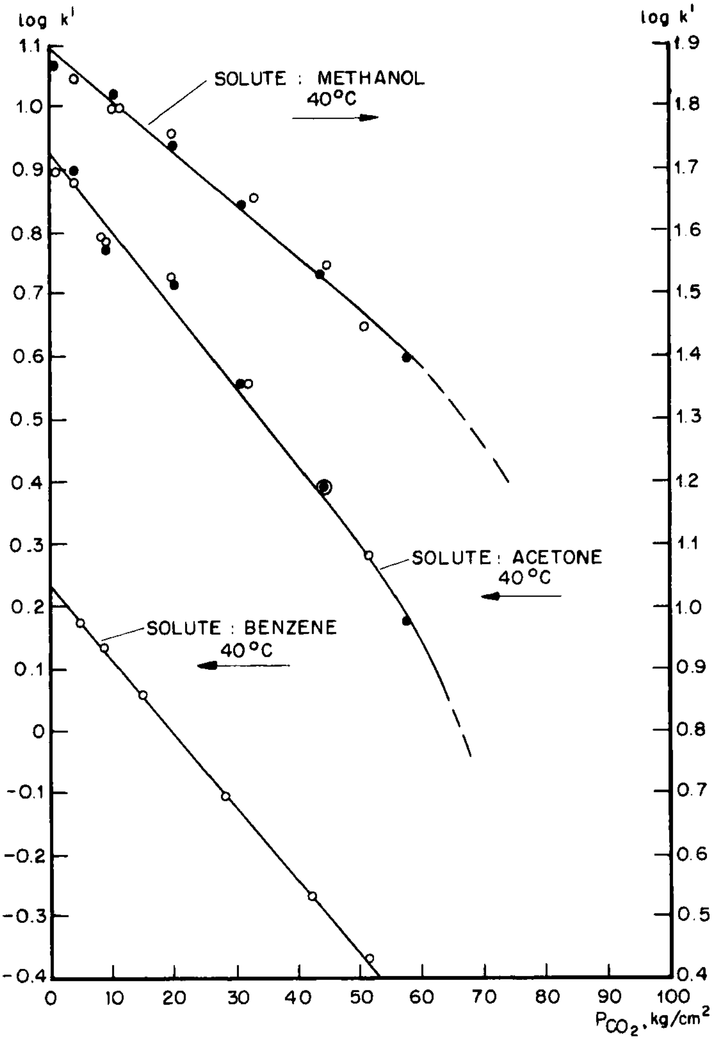

FIG. 8. Effect of CO_2 pressure on the partition coefficients of methanol, acetone, and benzene on a glycerol column.

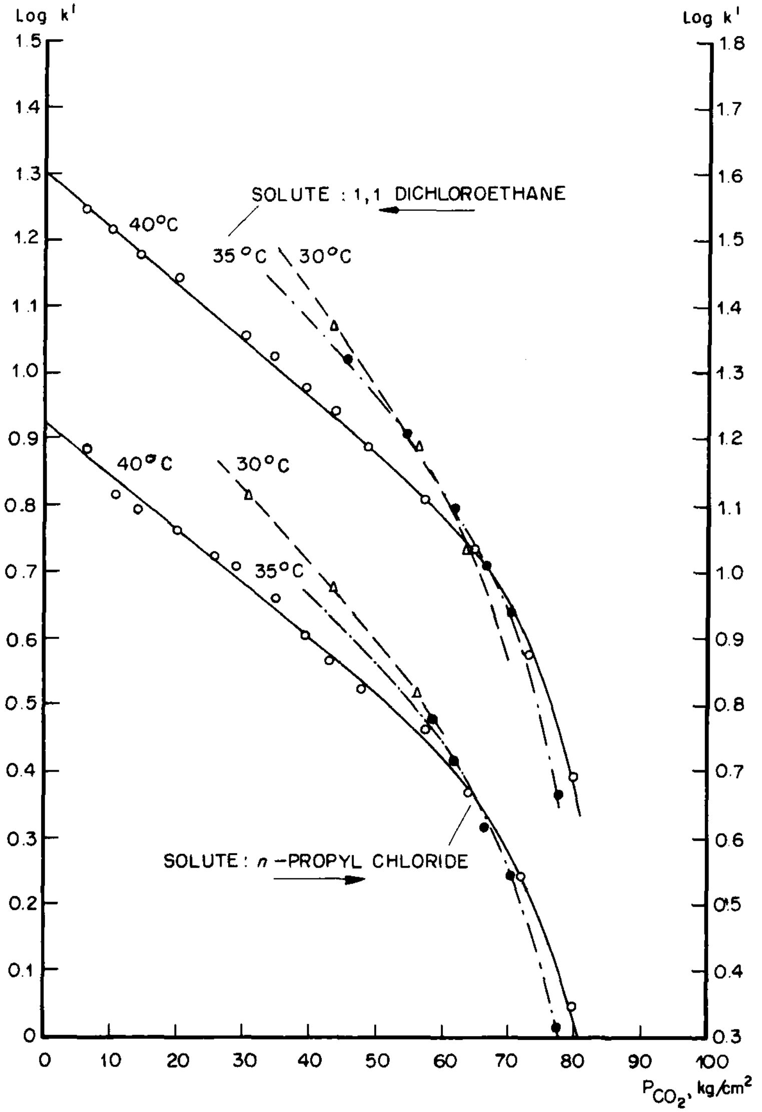

FIG. 9. Effect of CO_2 pressure on the partition coefficients of 1,1-dichloroethane and *n*-propyl chloride on a squalane column.

At a pressure of 60 atm, the molar amount of CO_2 dissolved is equivalent to less than 0.4% of the OH groups present. In this case we may expect the nature of the stationary liquid to be practically unchanged, which means that the large effect of pressure

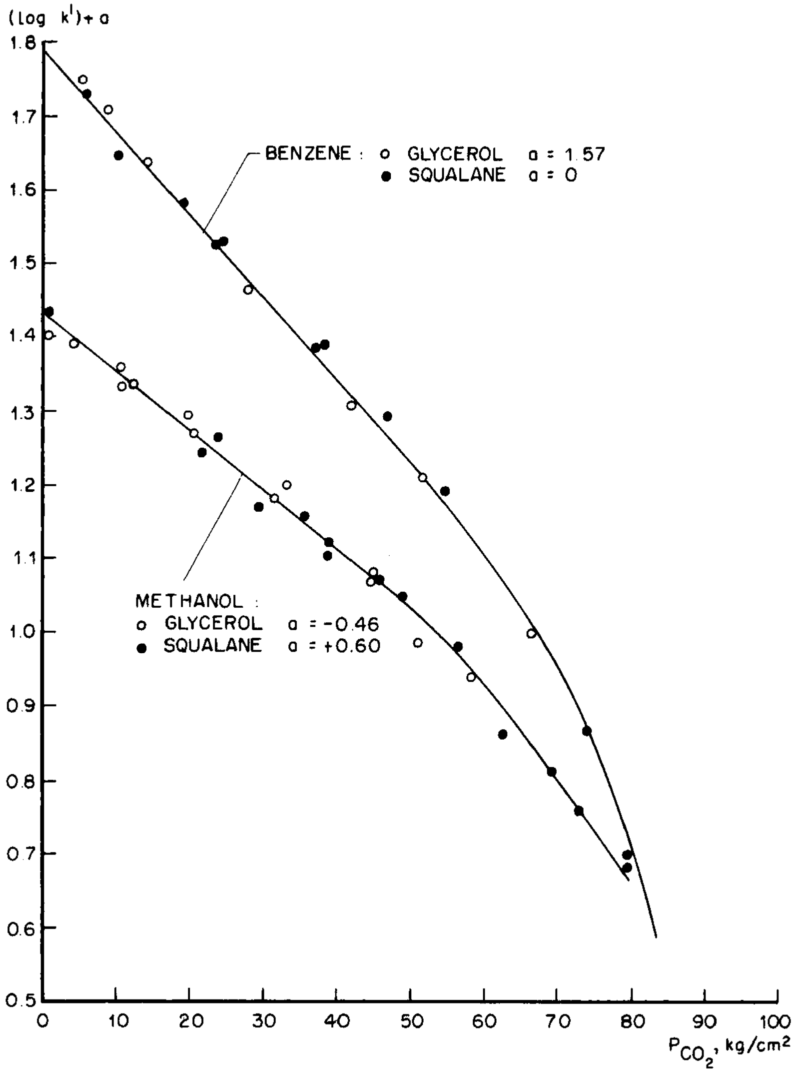

FIG. 10. Comparison of results on glycerol and squalane columns. $T = 40°C$.

on k' must be mainly due to molecular interactions in the gas phase and the mechanical pressure on the liquid.*

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* The fact that only a small amount of gas dissolves in the liquid is in itself no proof that the partition coefficient of a solute will not be affected by the dissolved gas. Such a change may be effected if strong interactions occur between solute

Comparing the log k' versus P curves for squalane and glycerol as stationary phases, we see that the relative change of k' is nearly identical for the same solute, irrespective of the stationary liquid (Figs. 6 to 8). This is more clearly illustrated by Fig. 10, where log k' is plotted on a sliding logarithmic scale, allowing the curves for different stationary phases to be superimposed. From this figure we can conclude that in the case of squalane, too, the solubility of CO_2 has played only a minor role.

Calculation of $B_{1,2}$ Values from Experimental Results

Neglecting the contribution of carbon dioxide solubility, $B_{1,2}$ values can be calculated from the initial straight-line portion of the log k' versus P plots with the aid of Eq. (30). If it is assumed that no volume change occurs when liquid solute is mixed with the stationary liquid, the partial molar volume of the solute can be taken as equal to the molar volume of the pure liquid solute. Although this assumption is certainly not exact,* no large errors are involved as V_2^0 is generally smaller than $2B_{1,2}$.

The $B_{1,2}$ values thus calculated are given in Table 1.

Comparison of Experimental $B_{1,2}$ Values with Theoretically Estimated Figures

The averaging rules represented in Eqs. (21) to (24) are valid for molecules behaving as spheres with interaction energies of the London dispersion type. This assumption obviously does not quite hold for the systems investigated. For C_3 to C_8 n-paraffins, for instance, it has been found [see Connolly and Kandalic (*12*)] that the Lennard-Jones formula, which assumes spherical symmetry,

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and molecules of dissolved gas. It would seem inconsistent, however, if we tried to explain the large change in k' merely by the small amounts of CO_2 dissolved in glycerol, for this would imply the assumption of strong interactions between CO_2 and solute molecules in the liquid phase while denying such effects in the gas phase. With glycerol, the concentration (moles per unit volume) of CO_2 is much higher in the gas phase than in the liquid phase.

* An estimate of the errors involved in the case of n-C_5 as a solute and squalane as a stationary liquid may be obtained from measurements on the volume change of mixing for n-alkanes differing in chain length. The excess molar volume of mixtures of n-alkanes differing widely in chain length, e.g., n-C_5/n-C_{16} or n-C_8/n-C_{32}, is (in an absolute sense) less than -3 cm^3/mole [see (*10,11*)].

TABLE 1

Comparison of Experimental Values of Second Virial Cross Coefficients with Values Predicted by the Principle of Corresponding States ($T = 40°C$)

	$B_{1,2}$, cm^3 mole^{-1}		
System	Exptl.	Calc. acc. to Eq. (25)	Calc. acc. to Eq. (26)
Propane/CO_2	− 99	−190	−193
n-Butane/CO_2	−153	−255	−254
n-Pentane/CO_2	−198	−309	−326
1,3-Butadiene/CO_2	−155	−234	−243
Benzene/CO_2	−288[a]	−336	−366
Methanol/CO_2	−236[a]	−173	−185
Ethanol/CO_2	−303	−241	−257
1,1-Dichloroethane/CO_2	−215	−288	−327
Acetone/CO_2	−343	−297	−303

[a] Mean value.

is less suited than the Kihara formula for the potential energy, which introduces molecular shapes other than spherical.

For a system consisting of a polar and a nonpolar molecule, the equations for averaging the interaction energies should also contain molecular parameters such as the dipole moment of the polar molecule (*13,14*).

In view of the above considerations, it is not to be expected that application of the principle of corresponding states will yield accurate figures for the present systems. Nevertheless, it seems worthwhile to investigate whether there is at least some agreement as to the order of magnitude with the experimental values.

The critical data used in the calculations are mainly taken from API research project 44 and from the International Critical Tables. Table 1 compares the calculated figures with the experimental values for 40°C. They prove indeed to be of the same order of magnitude. All $B_{1,2}$ values are negative, which is consistent with the working temperature being below the Boyle point ($\frac{8}{3}T^*$).

For the hydrocarbons and chlorinated hydrocarbons a systematic difference may be observed. Experimental values are algebraically higher than the theoretically predicted figures (i.e., deviations from ideality actually proved to be smaller than theoretical). Although for compounds other than permanent gases experimental B values may differ substantially [differences of 100 cm^3/mole are not uncommon among values for benzene, carbon tetrachloride, and chloroform (*15,16*)], the present discrepancies are too large to be accounted for by experimental inaccuracies. The precision of the gas chromatographically determined $B_{1,2}$ values is believed to be better than 20 cm^3/mole. It is probable, therefore, that the discrepancies result from the inadequacy of the principle of corresponding states for the present systems. The coefficients in Eqs. (25) and (26) have been determined by Guggenheim and McGlashan from virial coefficients of gases such as Ne, A, N_2, H_2, O_2, CO, CH_4, C_2H_6 and n-C_4H_{10}; they were chosen to give the best fit for $T = T^*$, $T = \frac{8}{3}T^*$, and $T = 8T^*$ (which temperatures are higher than the present ones).

In this connection it may be mentioned that $B_{1,2}$ data calculated from the low-pressure experiments of Desty et al. (*6*) also show a systematic deviation for systems of CO_2 and C_5-C_7 saturated hydrocarbons at 25°C. Values predicted by the corresponding-states principle are about 200 cm^3/mole lower (in an algebraic sense), hence deviate in the same direction as observed by us.

Comparison of Gas Chromatographic $B_{1,2}$ Data with Other Experimental Values of Analogous Systems

In view of the above discussions it seems to be more appropriate to compare our $B_{1,2}$ data with those of more analogous systems, measured by an independent technique. Prausnitz and Benson (*17*) have measured $B_{1,2}$ values for combinations of CCl_4, n-octane, toluene, and n-decane with hydrogen, nitrogen, and carbon dioxide at 50 and 75°C. More recently, Connolly (*18,19*) investigated systems obtained by combination of hydrogen or carbon monoxide with benzene, isooctane, and n-octane at 50, 75, and 100°C.

As no direct comparison is possible, the data above were compared on a corresponding-states basis (see Fig. 11). It is seen from Fig. 11 that the results can be represented reasonably well by a single function φ [see Eq. (20)]. This function differs from Eqs. (25) and (26) in giving algebraically higher $B_{1,2}$ values in the temperature range considered.

Effect of Temperature

In normal GLC, lowering the temperature means a decrease in solute volatility and hence an increase in k'. However, as the devi-

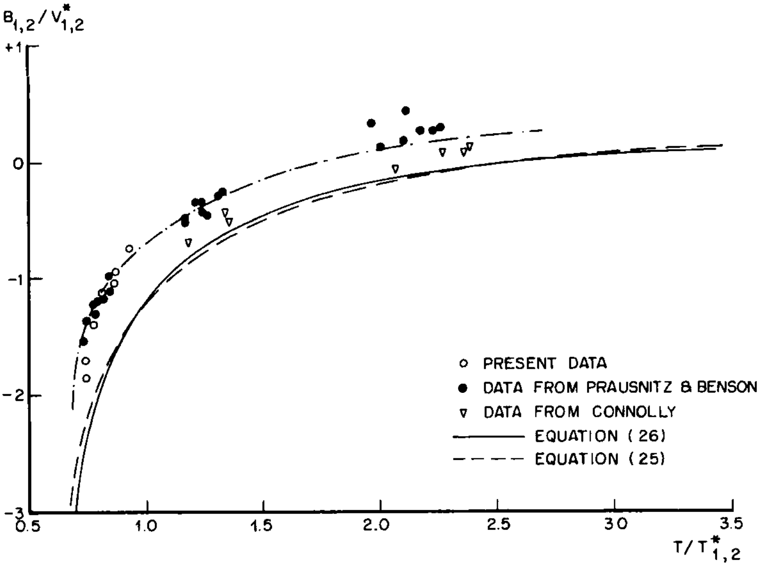

FIG. 11. Comparison of $B_{1,2}$ data for binary mixtures composed of a light gas and a hydrocarbon or chlorinated hydrocarbon on a corresponding-states-basis.

ations from ideality are more pronounced at lower temperatures (at least for temperatures below the Boyle point), the slope of the log k'-P graph is steeper. As can be seen in Figs. 4 to 7 and 9, for temperatures near the critical point the isotherms may cross at pressures slightly below the critical pressure of the carrier gas. Above the latter pressure the situation is reversed, a lower temperature causing a more rapid elution of the component.

Change of k' with Pressure for a Homologous Series

In normal GLC, the partition coefficients of members of a homologous series generally give rise to straight lines, if log k' is plotted against the molecular weight or the number of carbon atoms. This also applies to relative retention volumes or retention times, as these are proportional to k' values for a given set of gas chromatographic conditions.

Figures 12 and 13 show that the straight-line relationship also holds at higher pressures in the case of *n*-paraffins on a squalane column. This is not too surprising, as we may expect the second virial coefficients to change in a regular way on ascending a homolo-

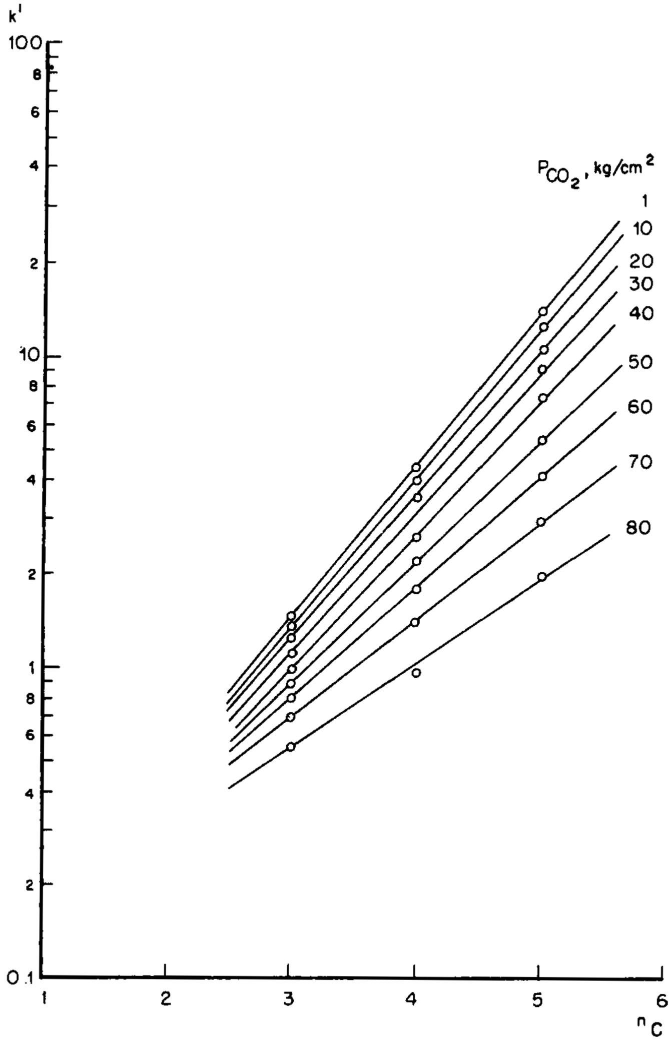

FIG. 12. Partition coefficients of some *n*-paraffins. Squalane column at 40°C.

gous series. As can be easily shown, $B_{1,2}$ values for systems composed of *n*-paraffins and CO_2 as calculated with the corresponding-states principle, can very well be represented by a linear function of paraffin chain length.

The additivity principle for the liquid molar volume is well known. Taking into account the pressure dependency of k' as

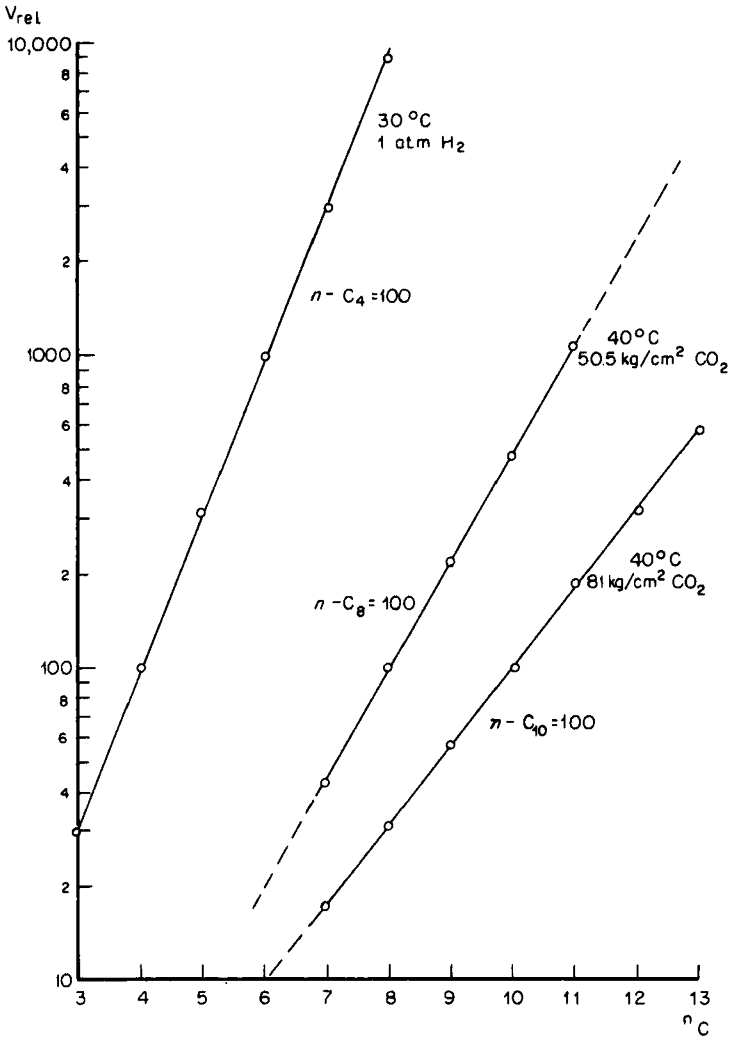

FIG. 13. Relative retention volumes for C_3-C_{13} normal paraffins. Squalane column.

given by Eq. (30), it is therefore understandable that the linear relationship between log k' and carbon number persists at higher pressures.

CONCLUSIONS

Application of High-Pressure Gas Chromatography to Nonanalytical Purposes

Collection of Equilibrium Data. High-pressure gas chromatography can be used as a convenient method for obtaining equilibrium data, e.g., for ternary systems comprising a gas, a relatively volatile compound, and a nonvolatile compound. Systems of this kind may be encountered in reservoir engineering, e.g., in connection with secondary recovery of oil (gas drive). Such equilibrium data are usually obtained by static methods (*20*), which are much more tedious, however.

In fact, since this work was undertaken, a few publications have appeared from workers at Rice University (Houston, Texas) dealing with determination of equilibrium data by a gas-chromatographic technique. Using a modified commercial GLC instrument, Stalkup and Kobayashi (*21*) have measured equilibrium data for methane/*n*-decane and some light hydrocarbons, and obtained good agreement with established data collected by classical methods. Recently, Gilmer and Kobayashi (*22*) have extended this study to gas-solid equilibria for a system composed of silica gel, methane, and C_2-C_4 *n*-paraffins.

Determination of Second Virial Cross Coefficients of Binary Mixtures

If the effect of carrier gas solubility is made negligible by suitable choice of the stationary liquid, high-pressure GLC may be an easy route toward $B_{1,2}$ values which are of considerable theoretical interest. $B_{1,2}$ values are normally obtained by accurate compressibility measurements on both the pure components and the mixture, or, alternatively, by measurement of the change of volume incident to mixing two gases (*23*). As pointed out by Lunbeck and Boerboom (*14*), both methods require a high degree of experimental accuracy. To determine the second virial coefficient of a single substance with an accuracy of 1%, compressibility measurements must be accurate to $1:10^4$, and even greater accuracy is necessary for $B_{1,2}$ determinations.

The required accuracy of $B_{1,2}$ values should be more easily attainable with the GLC technique. With the apparatus used in our study, the main source of scatter in the experimental k' values is believed to be inconstancy of flow; hence with a more sophisticated flow-control system a higher accuracy may well be attainable. However, the high-pressure gas-chromatographic technique seems to be somewhat limited with regard to choice of system and temperature range.

Analytical Applications of High-Pressure Gas Chromatography

The substantial drop in partition coefficient which can be realized by an increase in carrier gas density makes it possible to handle substances at lower temperatures than in normal gas chromatography. For instance, the k' value of benzene on a squalane column at a CO_2 pressure of 80 atm is lower by a factor of more than 10. As a rule of thumb, every 20 to 30°C temperature rise halves the retention time in normal GLC, which means that for this example the "gain in volatility" is roughly equivalent to a tem-

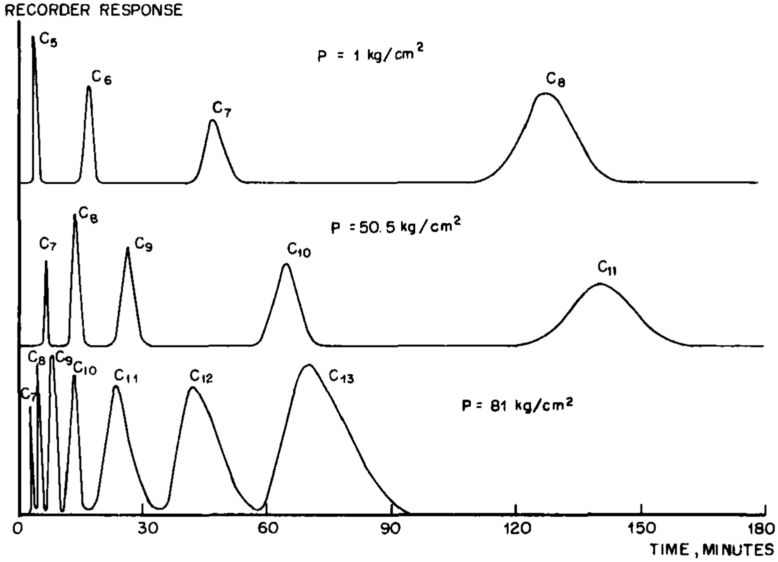

FIG. 14. Separations of *n*-paraffins on a squalane column at 40°C with CO_2 as a carrier gas at different pressures and comparable linear rates of mobile phase. Column: 1-m length of 3-mm-ID tube, filled with 25% w squalane on Sil-O-Cel 100/120 mesh. Sample size: approx. 15 μl of liquid mixture.

perature increment of about 100°C. Clearly, this may be of importance for the analysis of substances which decompose easily or for separations which require stationary liquids of low thermal stability.

As an illustration, Figs. 14 and 15 show some actual separations of a few hydrocarbons with the high-pressure technique. Although the character of a gas-chromatographic separation is retained, operation at higher pressure permits handling of heavier compounds.

An important feature of high-pressure gas chromatography can be deduced from Figs. 12 and 13. It is seen that the slope of the log k' versus n_c plots for a homologous series decreases at higher pressure. This means that the "gain in volatility" is relatively higher for heavy substances. In a sense, this is favorable, as the enhancement of volatility is primarily desired for heavier compounds. In another sense, however, we may regard the decrease in slope as a decrease in "light/heavy" selectivity, which means that the possibilities of separating neighboring members of a homologous series diminish with increasing pressure.

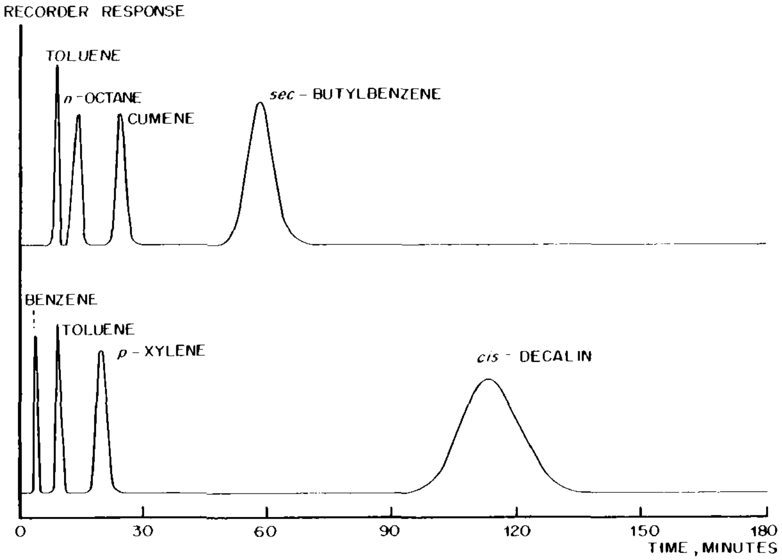

FIG. 15. Separations of some hydrocarbons on a squalane column at 40°C and 50.5 kg/cm^2 with CO_2 as a carrier gas. Column: 1-m length of 3-mm-ID tube, filled with 25% w squalane on Sil-O-Cel 100/120 mesh. Sample size: approx. 15 μl of liquid mixture.

The decrease in light/heavy selectivity also has a favorable aspect: It promotes the possibility of class separations in wide-boiling mixtures. This type of separation is more difficult to obtain in normal gas chromatography, especially for less volatile compounds (because selective liquids suitable for high-temperature operation are scarce and as the selectivity tends to decrease at higher temperatures). For such problems high-pressure GLC might well be a good solution. As an example, we may consider the selective separation of olefins from paraffins by means of a highly selective, although thermally instable liquid (such as a solution of silver ions in a polar solvent).

From the extremely rapid decrease of k' with increasing pressure near the critical point of the carrier gas the conclusion may be drawn that with pressures well above the critical value there may be a possibility of handling substances that lie beyond the limits of present-day gas chromatographic techniques. These possibilities will be demonstrated in a future paper.

Nomenclature

B	second virial coefficient
B_m	second virial coefficient of a mixture
$B_{1,1}$	second virial coefficient of component 1
$B_{2,2}$	second virial coefficient of component 2
$B_{1,2}$	second virial cross coefficient for a binary mixture
k	partition coefficient
$k'\left(=k\dfrac{V_L}{V_G}\right)$	capacity ratio
n_g	moles in gas phase
n_l	moles in liquid phase
P	pressure
P^+, P_0	reference pressures
R	gas constant
r	molecular distance
r^*	characteristic molecular dimension
$r^*_{1,1}$	characteristic molecular dimension, pertaining to a pair of molecules of type 1
$r^*_{2,2}$	characteristic molecular dimension, pertaining to a pair of molecules of type 2
$r^*_{1,2}$	characteristic molecular dimension, pertaining to

	a pair consisting of a molecule of type 1 and one of type 2
t_G	elution time of an inert gas
t_R	elution time of a solute
T	absolute temperature
T^*	characteristic temperature or critical temperature
$T^*_{1,1}$	critical temperature of component 1
$T^*_{2,2}$	critical temperature of component 2
$T^*_{1,2}$	characteristic temperature for a binary system
V	volume
V_g	gas volume
V_l	liquid volume
V_G	total gas volume in chromatographic column
V_L	total liquid volume in chromatographic column
V^*	critical volume
$V^*_{1,1}$	critical volume of component 1
$V^*_{2,2}$	critical volume of component 2
$V^*_{1,2}$	characteristic volume for a binary system
V_2	partial molar volume of component 2 in a liquid mixture
x	mole fraction of component 2 (solute) in liquid phase
y	mole fraction of component 2 in gas phase
ϵ^*	characteristic interaction energy
$\epsilon^*_{1,1}$	characteristic energy pertaining to the interaction of molecules of type 1
$\epsilon^*_{2,2}$	characteristic energy pertaining to the interaction of molecules of type 2
$\epsilon^*_{1,2}$	characteristic energy pertaining to the interaction of a molecule of type 1 with one of type 2
μ	chemical potential
μ_2	chemical potential of component 2 (solute)
μ_2^+	standard chemical potential of component 2 (solute)

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