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EFFECT OF PRESSURE DROP ACROSS THE COLUMN ON AVERAGE DENSITIES AND CAPACITY FACTORS IN SUPERCRITICAL FLUID CHROMATOGRAPHY

KEITH D. BARTLE, TERRY BODDINGTON, ANTHONY A. CLIFFORD* and GAVIN F. SHILSTONE

School of Chemistry, University of Leeds, Leeds LS2 9JT (U.K.)

SUMMARY

Calculations have been carried out of the average densities and capacity factors in supercritical fluid chromatographic (SFC) columns, taking into account the effect of the pressure drop along the column using, as examples, carbon dioxide as the mobile phase and phenanthrene as the solute. The values obtained were compared with those predicted for the mean pressure in the column. Differences are found which can be substantial for both the density and the capacity factor. Maximum deviations are found to move to higher pressures as the temperature rises. The effect of pressure drop needs to be taken into account by those using SFC to make quantitative measurements.

INTRODUCTION

In supercritical fluid chromatography (SFC) there will be a pressure drop across the column which will vary from around 1 bar for a short capillary column up to say 30 bar for some packed columns. Properties relevant to SFC, such as the density of the mobile phase, ρ , the dynamic viscosity, η , the capacity factor, k' , and the diffusion coefficient will vary with pressure along the column and do this more dramatically in the region of the critical point. The effect of pressure drop along a column in capillary SFC has been discussed theoretically by Peadar and Lee¹. They use a model in which the mobile phase pressure and density drop is linear with distance along the column. These approximations are less valid near the critical point, but the model does allow a comprehensive analysis of separation, efficiency and resolving power. Schoenmakers and Unk² have recently published an experimental and theoretical study of the effect of pressure drop on retention and efficiency in packed-column SFC using an alternative simple model. The present theoretical study is restricted to a discussion of average density and capacity factor, but uses a more exact treatment and experimentally based physical properties.

The capacity factor exhibited experimentally by a column and the density needed to convert retention times to retention volumes will be averages obtained by integration along the column. When quantitative measurements are made these are often referred to the mean pressure along the column, $p_{\text{mean}} = (p_{\text{in}} + p_{\text{out}})/2$, which assumes

that the pressure is dropping linearly with distance along the column, in a similar approach to those described above. The purpose of this paper is to test this model and compare the calculated true average density, $\langle \rho \rangle$, and capacity factor, $\langle k' \rangle$, with their respective values for the mean pressure for a model system: the chromatography of phenanthrene in carbon dioxide under various conditions. The work was carried out to test the validity of a quantitative study of the retention properties of polyaromatic hydrocarbons in packed-column SFC³, and data for phenanthrene obtained in this study are used as model data in the calculations given below. The results obtained are relevant whenever retention data are used to make quantitative physical property measurements, for example when supercritical fluid solubilities are obtained from chromatographic studies^{4,5}.

An asymptotic analysis of the problem of chromatography in a coated capillary column in which there is a pressure drop, and the parameters are an arbitrary function of pressure, has been carried out⁶. This shows that under typical chromatographic conditions, where the fractional change in pressure and the parameters which depend on it are small over a distance equal to the capillary radius, flow is essentially axial, and the formula given below are a very good approximation. A simpler and approximate derivation of the formulae is given here, which assumes axial flow and that the Poiseuille equation can be applied over short sections of the capillary. Although derived here for a uniform capillary column, the final results (eqns. 6 and 10) are approximately applicable to a packed column, where the pressure drop problem is more serious.

THEORY

According to Poiseuille's equation, the mean volume flow-rate, v , along a uniform cylindrical tube of radius a is given by

$$v = -(\pi a^4/8\eta)(dp/dl) \quad (1)$$

where dp/dl is the pressure gradient along the tube. The volume flow-rate varies along the tube as expansion takes place, but the mass flow rate, $m = \rho v$, is a constant. Substituting for v in eqn. 1 gives an equation for the pressure gradient,

$$dp/dl = -(8m/\pi a^4)(\eta/\rho) \quad (2)$$

The pressure falls non-uniformly along the tube determined by the dependence of the ratio η/ρ (the kinematic viscosity) on pressure. Some calculations of this ratio are presented below in Fig. 1. Rearrangement of eqn. 2 followed by integration over the column gives

$$m = (\pi a^4/8L) \int_{p_{\text{out}}}^{p_{\text{in}}} (\rho/\eta) dp \quad (3)$$

where L is the length of the column. Eqn. 3 gives a formula for the mass flow through

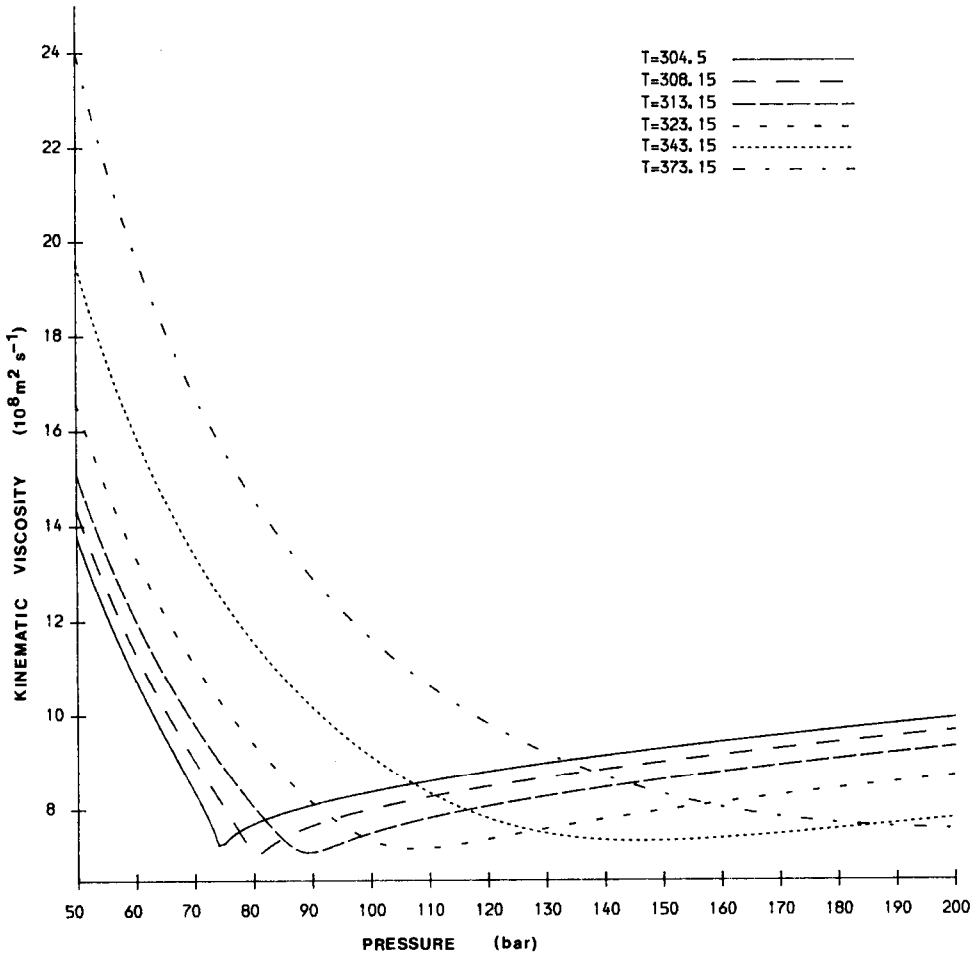


Fig. 1. Isotherms of the kinematic viscosity (η/ρ) as a function of pressure. The values are proportional to the pressure gradient (dp/dl) along a capillary. Temperatures in K.

a column in terms of its dimensions and a pressure integral of the properties of the mobile phase.

The average density in the column will be given by

$$\langle \rho \rangle = (1/L) \int_0^L \rho dl. \tag{4}$$

After substituting for dl , using eqn. 2, this becomes

$$\langle \rho \rangle = (\pi a^4 / 8mL) \int_{P_{out}}^{P_{in}} (\rho^2 / \eta) dp \tag{5}$$

and on substitution for m using eqn. 3 we finally obtain

$$\langle \rho \rangle = \int_{p_{\text{out}}}^{p_{\text{in}}} (\rho^2/\eta) dp \left[\int_{p_{\text{out}}}^{p_{\text{in}}} (\rho/\eta) dp \right]^{-1} \quad (6)$$

Turning now to the calculation of $\langle k' \rangle$, the linear average velocity of a solute in the column, dl/dt , will be given by $v/\pi a^2(1+k')$, and thus

$$dt = (\pi a^2(1+k')/v) dl = -[\pi a^2 \rho(1+k')/m](dl/dp) dp \quad (7)$$

After substituting for dl/dp using eqn. 2 and integrating over the length of the column, we obtain t_R , the retention time of the solute in the column;

$$t_R = (a^2/8m^2) \int_{p_{\text{out}}}^{p_{\text{in}}} [\rho^2(1+k')/\eta] dp \quad (8)$$

For an unretained solute as k' tends to zero t_R becomes t_M , the retention time of the mobile phase, and thus

$$t_M = (a^2/8m^2) \int_{p_{\text{out}}}^{p_{\text{in}}} (\rho^2/\eta) dp \quad (9)$$

The average capacity is given by $\langle k' \rangle = (t_R - t_M)/t_M$, or

$$\langle k' \rangle = \int_{p_{\text{out}}}^{p_{\text{in}}} (\rho^2 k'/\eta) dp \left[\int_{p_{\text{out}}}^{p_{\text{in}}} (\rho^2/\eta) dp \right]^{-1} \quad (10)$$

CALCULATIONS AND RESULTS

Data for the density of carbon dioxide were obtained from the IUPAC formulation⁷, and for the viscosity from an ESDU report⁸. Calculations were first carried out to obtain the ratio η/ρ , to which the pressure gradient along the column is proportional (eqn. 2), and these are plotted as isotherms in Fig. 1. Calculations were then carried out of the percentage deviations of the average density (as given by eqn. 6) from the density at the mean pressure, *i.e.*, $100(\rho(p_{\text{mean}}) - \langle \rho \rangle)/\langle \rho \rangle$. Results at 308.15 K, close to the critical temperature, are plotted as a function of pressure in Fig. 2 for a 5-bar and a 30-bar pressure drop along the column. A diagram of the surface of these deviations as a function of pressure and temperature is also given in Fig. 3 for a 30-bar pressure drop.

For calculations of $\langle k' \rangle$ some model data for k' as a function of pressure and temperature are required and these were obtained from published data³ for

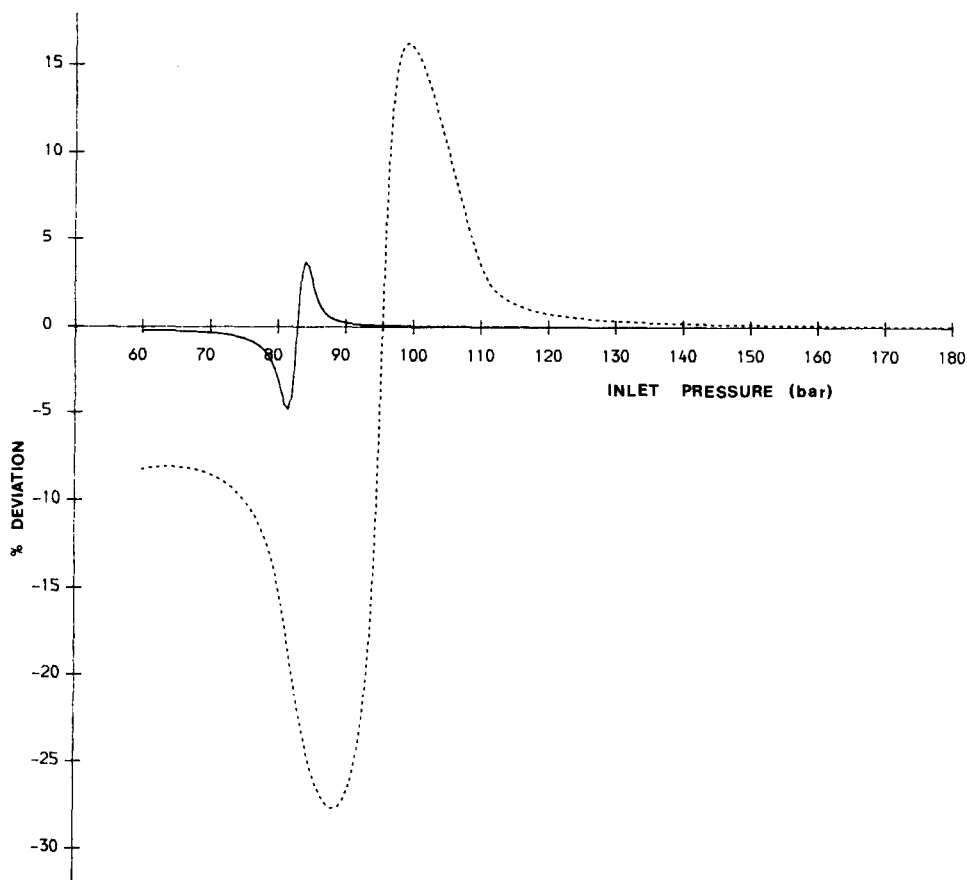


Fig. 2. Percentage deviation of the average density in a column from the density at the mean pressure, $100(\rho(p_{\text{mean}}) - \langle \rho \rangle) / \langle \rho \rangle$, as a function of inlet pressure at 308.15 K for a 5-bar (—) and 30-bar (---) pressure drop across the column.

phenanthrene in a 250 mm \times 4.6 mm I.D. ODS-2 column as follows. This study showed that the quantity $(\ln k' + \ln c - \ln \varphi)$, where c is the concentration of the supercritical fluid and φ the fugacity coefficient of the solute in the supercritical phase, is approximately a straight-line function of $1/T$. The linear relationship obtained for phenanthrene was used to back-calculate k' at any pressure and temperature, using c obtained from the density of pure carbon dioxide and φ obtained from the Peng-Robinson equation of state¹⁰ and the parameters given in the reference. An example of an isotherm of k' versus pressure at 328.15 K is given in Fig. 4. This can be compared with experimental isotherms for similar compounds¹⁰ and shows that it is reasonable model data.

Calculations were then carried out, using eqn. 10, of the percentage deviation of the average capacity factor over a column from the capacity factor at the mean pressure, i.e. $100(k'(p_{\text{mean}}) - \langle k' \rangle) / \langle k' \rangle$. These deviations are plotted at 308.15 K as a function of pressure in Fig. 5, for a 5-bar and a 30-bar pressure drop along the

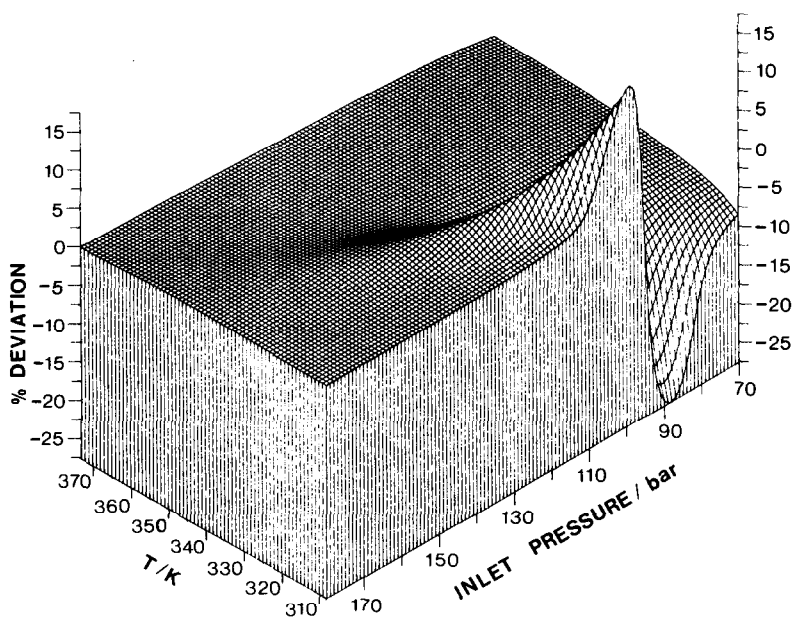


Fig. 3. Percentage deviation of the average density in a column from the density at the mean pressure, $100(\rho(p_{\text{mean}}) - \langle \rho \rangle) / \langle \rho \rangle$, as a function of inlet pressure and column temperature for a 30-bar pressure drop across the column.

column. A diagram of the surface of these deviations as a function of pressure and temperature is also given in Fig. 6 for a 30-bar pressure drop.

DISCUSSION

The pressure gradient along the column, according to eqn. 2, is proportional to the kinematic viscosity η/ρ . The curves on Fig. 1 therefore show how the pressure gradient (dp/dl) varies along a column as the pressure changes at various temperatures from 31.35°C (just above the critical temperature) to 100°C. Considering a long capillary, where the pressure fell from 100 bar to 50 bar, we can see that the pressure would fall fairly uniformly along the tube at first, but that the rate of fall would slow down to a minimum. The pressure gradient would then rise rapidly towards the end of the tube as the fluid becomes more gas-like. The minimum of dp/dl is near the critical pressure at a temperature close to the critical temperature, but rises to higher pressures (*i.e.*, towards more typical SFC pressures) as the temperature rises.

Figs. 2 and 3 show deviations of the average density from the density at the mean pressure. These are greatest at the lowest temperature, being around 25% for a 30-bar pressure drop among the column and a few percent for a 5-bar drop. The deviations fall off as the temperature rises, but move to higher pressures reflecting the behaviour of the minima in the kinematic viscosity curves.

Capacity factors change over several orders of magnitude over the range 70 bar to 170 bar as can be seen in the example for phenanthrene in Fig. 4. More dramatic

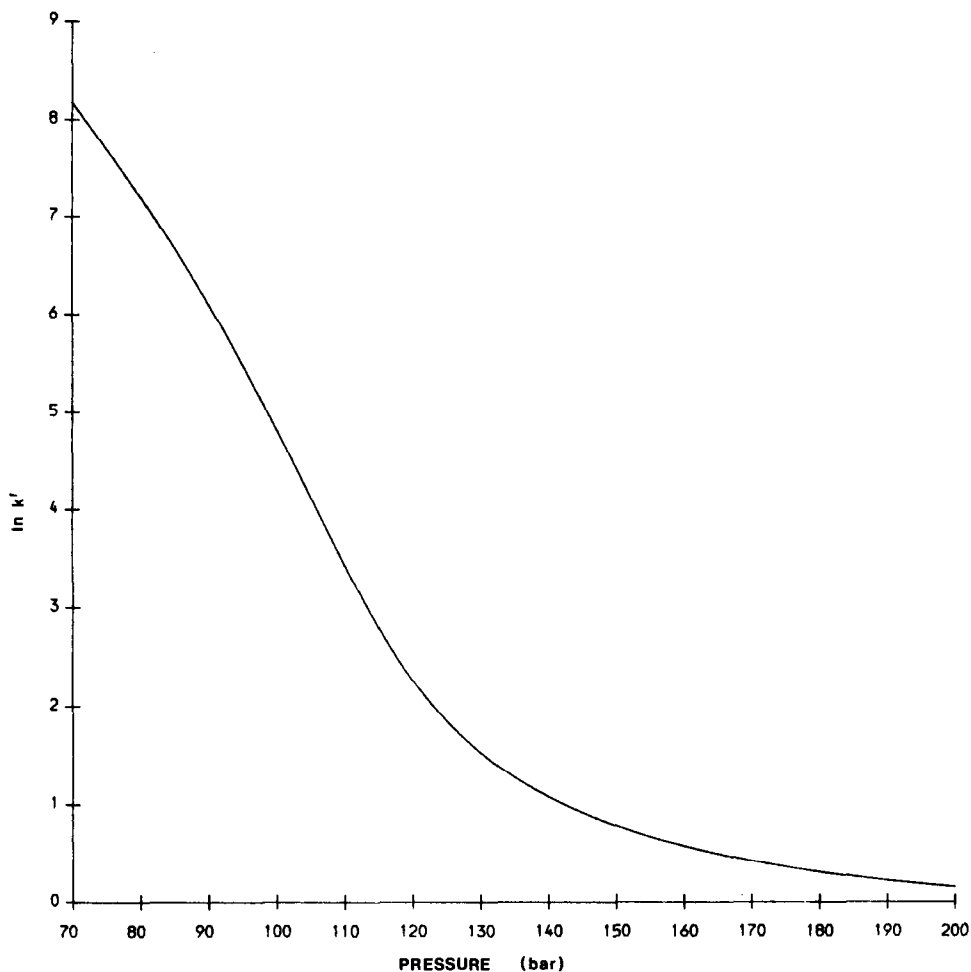


Fig. 4. An example of model data for the retention of phenanthrene by an ODS-2 column using carbon dioxide at 308.15 K: the natural logarithm of the capacity factor, $\ln k'$, is plotted as a function of pressure.

deviations are consequently obtained between the capacity factor observed over a column with pressure drop and that predicted for the mean pressure. At 35°C deviations of 90% are calculated for a 30-bar pressure drop over the column and even 40% for a 5-bar drop as shown on Fig. 5. Fig. 6, the three-dimensional diagram, shows a wide ravine again moving to higher pressures as the temperature rises.

These calculations for the system carbon dioxide and phenanthrene illustrate the extent of the effects which arise from the non-linear drop in pressure among an SFC column, which need to be considered by those attempting to make quantitative measurements using SFC. As would be expected, the very large effects are around the mobile phase critical point, but they do extend some way from it and in an unsymmetrical way, such that they are not inconsiderable for the model system at

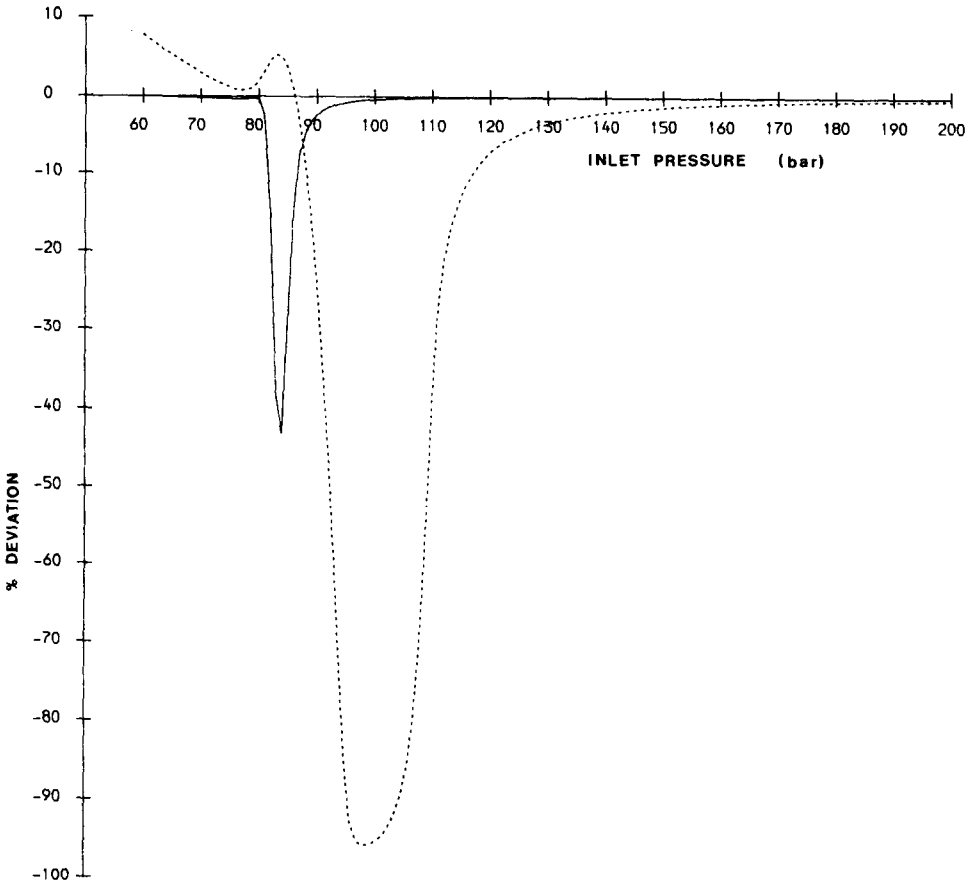


Fig. 5. Percentage deviation of the observed capacity factor, for columns with 5-bar (—) and 30-bar (---) pressure drops across the column, from the capacity factor calculated for the mean pressure, $100(k'(p_{\text{mean}}) - \langle k' \rangle) / \langle k' \rangle$, as a function of inlet pressure at 308.15 K.

a temperature of 70°C and a pressure of 150 bar, well above the critical values for carbon dioxide.

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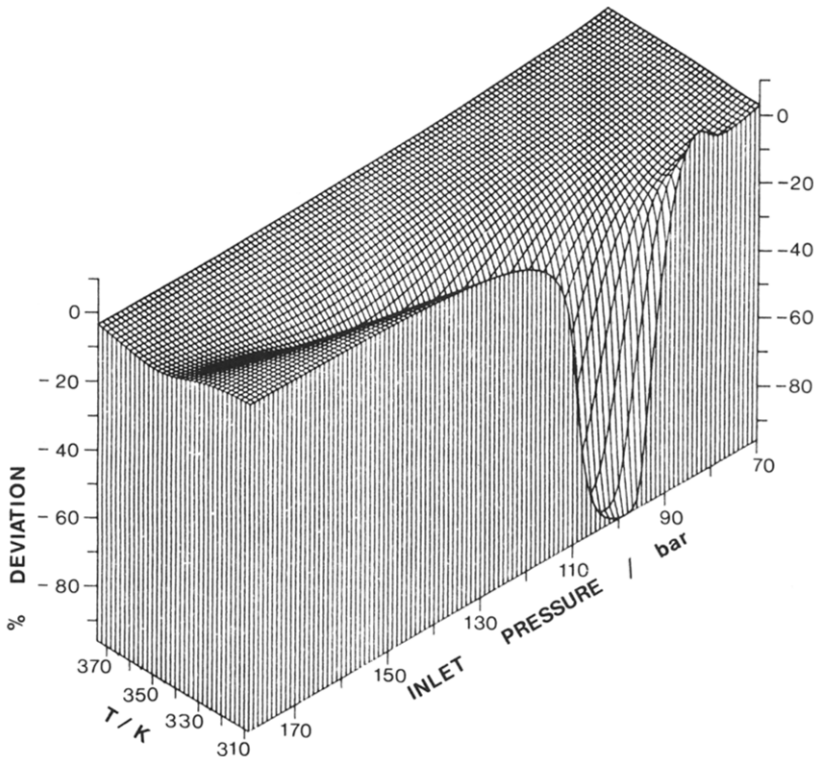


Fig. 6. Percentage deviation of the observed capacity factor for a column with a 30-bar pressure drop from the capacity factor calculated for the mean pressure, $100(k'(p_{\text{mean}}) - \langle k' \rangle) / \langle k' \rangle$, as a function of inlet pressure and temperature.

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