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PRESSURE DEPENDENCE OF THE COEFFICIENTS OF MASS-TRANSFER RESISTANCE IN GAS CHROMATOGRAPHY

J. NOVÁK, S. WIČAR AND P. BOČEK

Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Science, Brno (Czechoslovakia)

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SUMMARY

The liquid and gas-phase mass-transfer resistance coefficients have been evaluated from HETP *versus* carrier gas flow velocity ($\bar{u}$) measurements carried out at different absolute column pressure ($\bar{P}$) levels. The C_s coefficients in the liquid-phase mass-transfer term ($C_s\bar{u}$), as obtained by measuring the HETP increments of a constant $\bar{P}\bar{u}$, were increasing upon raising the pressure level, while the respective C_m coefficients in the gas-phase mass-transfer term ($C_m\bar{P}\bar{u}$) displayed a decrease. Both C_s and C_m coefficients decreased with increasing carrier gas flow velocity. The above situation indicates that the liquid and gas-phase mass-transfer terms are dependent on each other.

INTRODUCTION

The rate theory expressed by either $\bar{H} = A + B/\bar{P}\bar{u} + C_m\bar{P}\bar{u} + C_s\bar{u}$ or by $\bar{H} = [1/(1/A + 1/C_m\bar{P}\bar{u}] + B/\bar{P}\bar{u} + C_s\bar{u}$ (where the symbols have the usual meaning), predicts that the coefficients of mass-transfer resistance, C_m and C_s, are independent both of each other and of $\bar{P}$ and $\bar{u}$. However, PERRETT AND PURNELL[1] found the C_m term to be generally dependent on the inhomogeneity of the liquid phase film. On the other hand, SAHA AND GIDDINGS[2] found a dependence between the C_s coefficient and the diameter of the support particle. Thus, the mobile-phase mass-transfer resistance coefficient seems to be a function of a parameter typical for the liquid-phase mass-transfer resistance coefficient, the latter being, in turn, dependent on a parameter controlling the mass transfer in the mobile phase.

This indicates that there is some kind of interdependence between the coefficients C_m and C_s; a theoretical substantiation of this concept has been presented in another paper[3]. The present paper is to demonstrate a phenomenon that appears to be associated with the above situation — a dependence of the coefficients C_s and C_m on the absolute column pressure and on the mobile phase flow velocity. This phenomenon was disclosed by virtue of obtaining systematically inconsistent results in the isolation of the C_s and C_m coefficients from HETP *versus* carrier gas flow velocity measurements carried out at various levels of the mean absolute column pressure on packed columns[4].

CALCULATION OF THE C_s AND C_m COEFFICIENTS

A computer program for the least square fitting of the equation $\bar{H} = A + B/\bar{P}\bar{u} + C_m\bar{P}\bar{u} + C_s\bar{u}$ to the experimental data obtained at different column pressures failed; frequently negative values were obtained for the C_m coefficients, though a large number of precisely measured data had been processed. Therefore, we employed the graphical method of GIDDINGS AND SCHETTLER[5] of measuring the $\bar{H}/f_1$ increments of a constant X.

This method was originally proposed for processing HETP *versus* column outlet flow velocity data obtained either with various kinds of carrier gas or at different levels of the column outlet pressure, with a given carrier gas. As we disposed of a lot of HETP *versus* average flow velocity data obtained on columns of different lengths at various levels of either constant column outlet pressure or constant column inlet pressure and related to the mean column pressure, we have modified the original formulation of the method to make it suitable for readily processing the above kind of data.

The original version[5] has been based on the relation

$$\frac{\bar{H}}{f_1}(X) = \bar{H}_m(X) + C_s X D_m' f_2/P_o f_1 \tag{1}$$

where $\bar{H}$ is the apparent plate height, $\bar{H}_m$ is the sum of the mobile phase terms, X stands for $u_o P_o/D_m'$ where u_o is the carrier gas velocity at the column outlet, P_o and D_m' are the column outlet pressure and the solute diffusion coefficient in the gas phase at a unit pressure, respectively. f_1 is the decompression factor given by $f_1 = (9/8)(P^4 - 1)(P^2 - 1)/(P^3 - 1)^2$ where P is the column inlet-to-outlet pressure ratio, and f_2 is the well-known James–Martin factor.

Since $P_o u_o = \bar{P}\bar{u}$, $\bar{D}_m\bar{P} = D_m'P'$, and $u_o = \bar{u}/f_2$, where $\bar{P}$ and P' are the mean column pressure and a unit pressure, respectively, and $\bar{D}_m$ is the solute diffusion coefficient in the mobile phase at the mean column pressure, one can write with reference to the fundamental GIDDINGS' papers[6]

$$\bar{H} = \left(A + \frac{2\gamma D_m'P'}{\bar{P}\bar{u}} + \frac{\omega d_p^2}{D_m'P'}\bar{P}\bar{u}\right) f_1 + C_s\bar{u} \tag{2}$$

Hence, eqn. 1 may be rearranged to read

$$\frac{\bar{H}}{f_1}(X) = \bar{H}_m(X) + C_s X D_m'/\bar{P} f_1 \tag{3}$$

where X is given by $\bar{P}\bar{u}/D_m'$, which is obviously equivalent to the above $P_o u_o/D_m'$. The product $\bar{P}f_1$ may be expressed with the aid of STERNBERG AND POULSON'S[7] form of f_1, $(P_i^2 + P_o^2)/2(\bar{P})^2$, where P_i is the column inlet pressure.

Following the originally proposed procedure, C_s may be expressed by

$$C_s = \Delta\left[\frac{\bar{H}}{f_1}(X)\right]/X\Delta(D_m'/\bar{P}f_1) \tag{4}$$

where the Δ's designate the differences between the respective items, obtained by measurement for a given X at two different values of $\bar{P}$ or D_m'. In our case, the kind of carrier gas (H_2) remained unchanged and the mean column pressure was varied by changing parametrically either the outlet or the inlet column pressure, or, in one case, by changing the column length. Therefore, we chose $X = \bar{P}\bar{u}$, which renders

$$\frac{\bar{H}}{f_1}(X) = \bar{H}_m(X) + C_s X/\bar{P}f_1$$

and

$$C_s = \Delta\left[\frac{\bar{H}}{f_1}(X)\right]/X\Delta(1/\bar{P}f_1) \tag{5}$$

The C_m coefficient ($\omega d_p^2/D_m'P'$) was calculated from

$$C_m = \left[\frac{\bar{H}}{f_1}(X) - (C_s X/\bar{P}f_1)\right]/X \tag{6}$$

provided the respective experimental data have been obtained in a flow region dominated by the mass-transfer terms.

EXPERIMENTAL

The measurements were carried out on 3- and 0.75-m-long columns of 3 mm I.D., made of stainless-steel and packed with two sorts of packing — 25 and 3 wt.% of dinonyl phthalate on Chromosorb P 60/80 mesh. A Becker Multigraph 409 (Becker, Delft, The Netherlands) was employed in its version with thermal conductivity detection, adapted for work under controlled column outlet pressure. Hydrogen was used as the carrier gas.

With the high and the low liquid load packing, pentane and hexane were used as the solutes, respectively, the samples being introduced in the form of about 40 μl of the solute vapors diluted in hydrogen containing traces of air. A Zimmermann syringe was employed (Zimmermann, G. D. R.). In all cases the column as well as the injection port and the detector were kept at 40°. The chromatograms were recorded by a Servogor RE 512 recorder (Goerz Electro G.m.b.H., Austria). A more detailed description of the experimental conditions has been given in a previous paper[4].

RESULTS AND DISCUSSION

The results of the measurements were processed by plotting against the flow velocity the C_s and C_m values obtained for different levels of the mean column pressure. The above plots were complemented by the corresponding $\bar{P}$ *versus* flow velocity data.

The C_s and C_m *versus* $\bar{u}$ curves in Fig. 1 were obtained from the $\bar{H}/f_1$ *versus* $\bar{P}\bar{u}$ data measured with the 25% liquid load packing on the 0.75-m column operated at constant outlet pressures of 1 and 3 atm (columns a and c, respectively) and on the 3-m column operated at an outlet pressure of 1 atm (column b). As for the mean column pressure levels, the longer column (b) was chosen as a reference one (*cf.* the $\bar{P}$ *versus* $\bar{u}$ curves in Fig. 1), *i.e.*, the data for the C_s(a,b) and C_m(a,b) curves were obtained from the $\bar{H}/f_1$ and $1/\bar{P}f_1$ *versus* $\bar{P}\bar{u}$ measurements carried out on columns a and b, while the C_s(b,c) and C_m(b,c) correspond, analogously, to the measurements on columns b and c. The individual $\bar{H}/f_1$ and $1/\bar{P}f_1$ increments were read out in steps given by the experimental points on the $\bar{H}/f_1$ and $1/\bar{P}f_1$ *versus* $\bar{P}\bar{u}$ curves for the reference column; the flow velocities incidental to the individual C coefficients were determined from the respective $\bar{P}\bar{u}$ and $\bar{P}$ data.

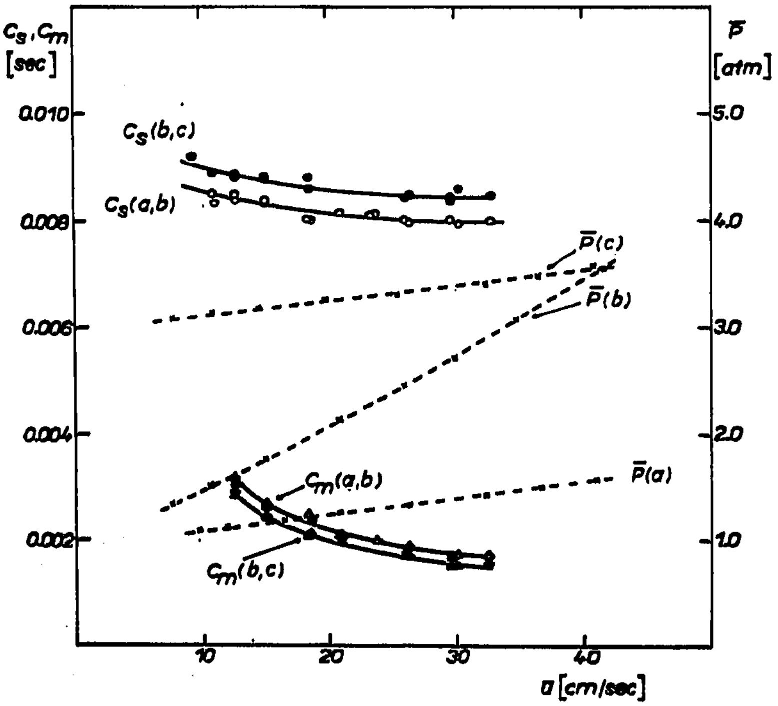

Fig 1. Flow velocity dependence of the coefficients C_s and C_m at two different absolute column pressure ($\bar{P}$) levels (constant column outlet pressure operation). a and c, 0.75-m-long column operated at 1 and 3 atm outlet pressure, respectively. b, 3-m-long column operated at 1 atm outlet pressure; column packing, 25 wt.% dinonyl phthalate on Chromosorb P 60/80 mesh at 40°; solute, pentane.

When accepting the arithmetic means of the absolute pressures in columns a and b and in columns b and c as approximate levels incidental to the corresponding C coefficients, one may infer from Fig. 1 that an increase in the absolute column pressure by about 1 atm leads to an increase in the C_s coefficient by about 0.0004 sec, while the C_m coefficient decreases by about 0.0002 sec under the same circumstances. Both the C_s and C_m coefficients show a pronounced decrease upon rising the flow velocity. As an increase in the flow velocity has associated with it an increase of the mean column pressure in this mode of column operation, the above situation indicates that the C_s coefficient decreases with increasing flow velocity.

The fall-off of the decrease of the C_s coefficients with increasing flow velocity may be explained by the counteracting effect of increasing column pressure; this account is supported by the results obtained on columns operated at constant inlet pressures and variable outlet pressure (*cf.* Fig. 2) where the increasing flow velocity leads to a fall of the column pressure.

Fig. 2 represents the results obtained with the same packing as mentioned in the previous case, but only with the 0.75-m-long column operated at three different inlet pressures, namely, 3.0, 3.6, and 5.5 atm (columns d, e, and f, respectively). The results were processed in the same way as described with Fig. 1; the reference results were those obtained on the column operated at 3.6 atm inlet pressure.

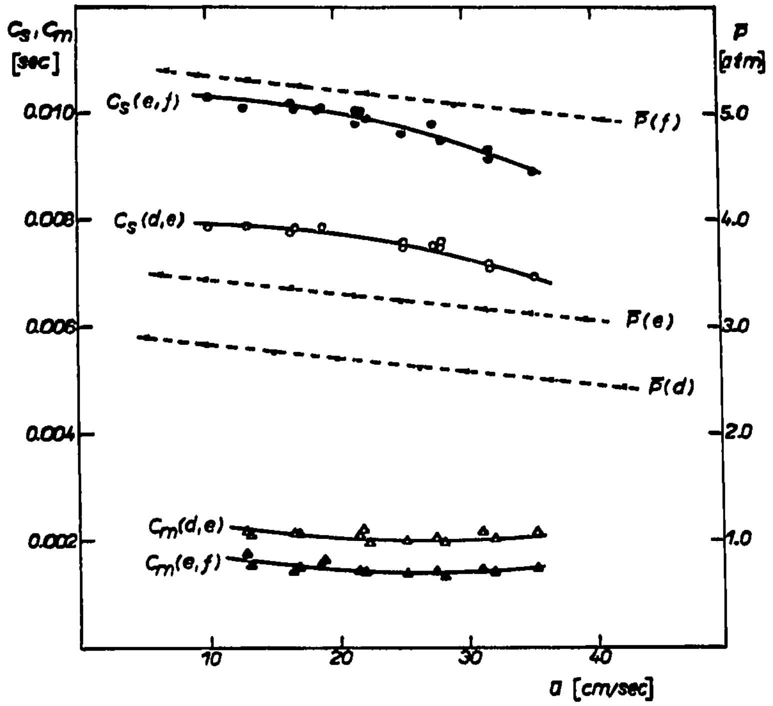

Fig. 2. Flow velocity dependence of the coefficients C_s and C_m at two different absolute column pressure ($\bar{P}$) levels (constant column inlet pressure operation). d, e and f, 0.75-m-long column operated at 3.0, 3.6, and 5.5 atm inlet pressure, respectively; column packing, 25 wt.% dinonyl phthalate on Chromosorb P 60/80 mesh at 40°; solute, pentane.

In this case, the pressure effects on both the C_s and C_m coefficients are higher than in the preceding case. Using again the above concept on the column pressure levels, a pressure increase by about 1.25 atm results in an increase of the C_s coefficients by about 0.002 sec and in a decrease of the C_m coefficients by about 0.0006 sec. The higher effect of the column pressure in this case may be due to the fact that all the measurements at the constant column inlet pressures have been carried out in a region of appreciably higher pressures (2.5–5.5 atm) as compared with those obtained at the constant outlet pressures (1–3.5 atm).

Contrary to the case with the constant column outlet pressures, the decrease of the C_s coefficients grows steeper upon raising flow velocity.

The relationship between the courses of the C_m curves obtained from the measurements under the constant outlet and the constant inlet pressures indicate that also the C_m coefficients show a decrease with increasing flow velocity. However, the present results are not apt for isolating the net flow-velocity contribution to the change of the C_s and C_m coefficients.

Fig. 3 shows the C_s and C_m *versus* $\bar{u}$ curves obtained from the data measured with the low liquid load packing on the 0.75-m-long column operated at constant column outlet pressures of 1 and 3 atm (column g and h, respectively). These results are supplemented by the results obtained with the same column and within approximately the same column pressure region, but with the high liquid load packing (Fig. 4). Apart from the obvious difference between the respective C_s coefficients, the comparison of the C_m curves in Figs. 3 and 4 shows an increase of the C_m coefficients upon the increase in the stationary liquid loading as described earlier by others[1], despite having injected pentane in this case.

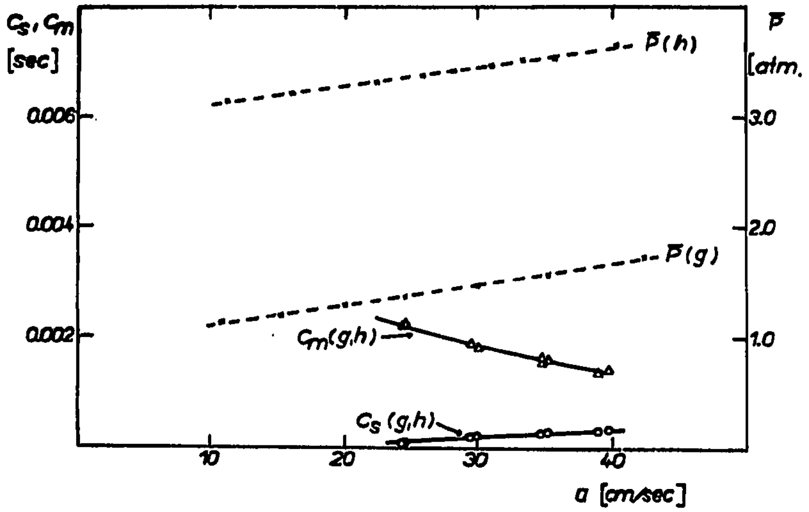

Fig. 3. Flow velocity dependence of the coefficients C_s and C_m (constant column outlet pressure operation). g and h, 0.75-m-long column operated at 1 and 3 atm outlet pressure, respectively; column packing, 3 wt.% dinonyl phthalate on Chromosorb P 60/80 mesh at 40°; solute, hexane.

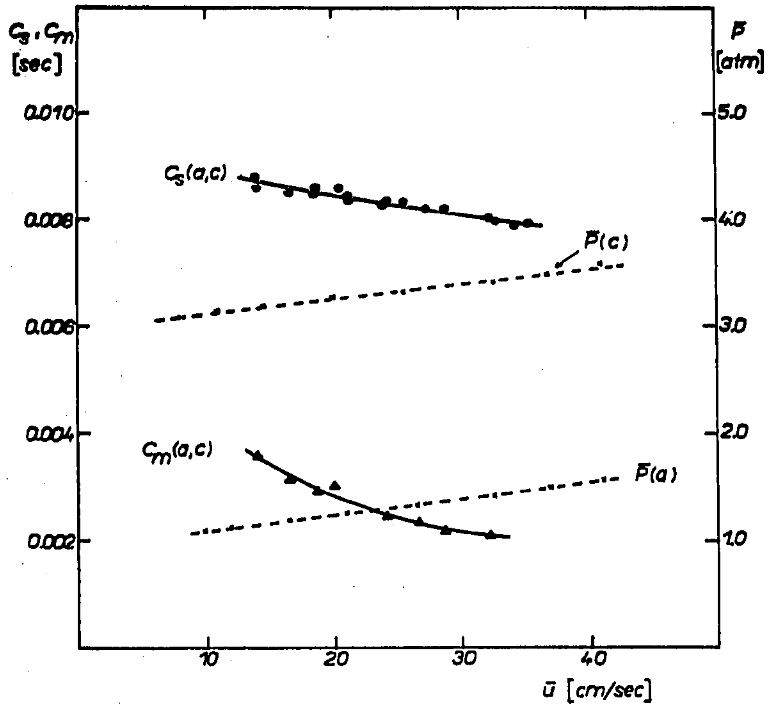

Fig. 4. Flow velocity dependence of the coefficients C_s and C_m (constant column outlet pressure operation). a and c, 0.75-m-long column operated at 1 and 3 atm outlet pressure, respectively; column packing, 25 wt.% dinonyl phthalate on Chromosorb P 60/80 mesh at 40°; solute, pentane.

CONCLUSIONS

The coefficients of the resistance to mass transfer in the liquid and in the gaseous phase appear to be functions of the column pressure and the mobile phase flow velocity. The liquid-phase mass-transfer resistance coefficient, as determined from the HETP, $\bar{P}$, $\bar{u}$ measurements by conventional methods, increases with increasing mean column pressure, while the gas-phase mass-transfer coefficient (defined by $C_m = \omega d_p^2/D_m'P'$, ref. 6), determined from the same measurements, decreases with increasing column pressure. Both the C_s and C_m coefficients decrease with increasing carrier gas flow velocity.

It follows from the pressure and flow velocity dependences of the coefficients C_s and C_m that the sum of the gas phase contributions to the HETP is not invariable with the position along the column and that the local liquid phase contribution, $C_s u$, rises not as steeply with increasing distance from the column inlet as it would be given by the growth of the flow velocity in a column operated at a constant outlet pressure. This indicates that it is hardly possible to separate accurately the coefficients C_m and C_s by the conventional methods, despite carrying out the corrections for the gas decompression effects[5,8].

The pressure dependence of the C_s coefficient may also play some role in the dependence of the HETP on the column length and the column pressure, especially with high liquid load packings. One can expect a less pronounced decrease of the minimum HETP and a more expressive rise of the steepness of the ascending branch of the HETP *versus* $\bar{u}$ curve upon increasing the column length or the column pressure than it would be encountered if the C_s coefficient were a constant independent of pressure, with columns operated at a constant outlet pressure. Nevertheless, it has followed from a previous paper[4] that these effects are practically insignificant under current conditions.

As it is hardly imaginable that the C_s coefficient might be directly affected by the pressure, it may be assumed that the pressure dependence of the mass transfer in the liquid phase is rooted actually in the pressure dependence of the mass transfer in the gaseous phase, *i.e.*, that the gas and liquid-phase mass-transfer terms are coupled with each other (*cf.* ref.3).

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