

## Gas chromatographic methods for the assessment of binary diffusion coefficients for compounds in the gas phase

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### ABSTRACT

Binary diffusion coefficients,  $D_g$ , were calculated for a number of compounds by using three gas chromatographic methods. All three methods showed good agreement when  $D_g$  was extrapolated to zero gas velocity. For the compounds tested, all  $D_g$  values were lower than those achieved by using the Fuller–Schettler–Giddings equation.

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### INTRODUCTION

Diffusion of compounds present in gases or air plays an important role in many chemical and physical processes. Relationships which govern the diffusion have been studied mathematically and empirically over a long period. The diffusion rate is described by individual diffusion coefficients that take into account chemical structure, temperature, viscosity, etc. So far, no method has been described that makes possible the exact calculation of binary diffusion coefficients, although a large number of empirically derived equations based on various methods have been published [1–9]. Thus, diffusion coefficients can be calculated roughly and simply, yielding errors that sometimes exceed 30%. Some equations are better adapted to certain environmental conditions, such as low molecular weight and moderate temperatures, depending on the empirical values available at the time of the formulation of the equation. In 1965, Fuller and Giddings [10] critically reviewed and tested the existing equations. They concluded that the Fuller–Schettler–Giddings (FSG) relationship was so far the best available general equation when utilized for the calculation of diffusion coefficients for a large number of compounds, covering as many applications as possible. Since then, the FSG equation has been commonly used with reference to the original paper [11]. In chromatography, the diffusion coefficients of specific compounds, in particular environments, are of great importance for the chromatographic process. Thus, for the relationship giving the height equivalent to a theoretical plate (HETP or H), diffusion coefficients for a compound in both the mobile and the stationary phase are used. For open-tubular gas chromatography, this relationship is given by [12]

$$H = 2D_{g0}f_1/v_0 + [C_{g0}f_1 + (C_1 + C_i)f_2]v_0 \quad (1)$$

where  $v_o$  is the carrier gas velocity at the outlet of the tube. The  $C$  terms represent the contributions due to resistance to mass transfer in the gas phase (g), liquid phase (l) and the interface (i):

$$C_{go} = \frac{r^2(11k'^2 + 6k' + 1)}{24(1 + k')^2 D_{go}} \quad (2)$$

where  $r$  is the tube radius,  $k'$  the capacity factor and  $D_{go}$  is the solute diffusion coefficient in the gas phase at the outlet gas velocity, and

$$C_l + C_i = \frac{2k'd_f}{(1 + k')^2} (d_f/3D_l + 1/k_d) \quad (3)$$

where  $d_f$  is the film thickness,  $D_l$  the diffusion coefficient in the liquid phase and  $k_d$  is the desorption rate constant. The  $C_i$  term is not regarded as being governed by diffusion. The pressure drop is taken into account by the  $f$  factors [13,14]:

$$f_1 = \frac{9(P^4 - 1)(P^2 - 1)}{8(P^3 - 1)^2} \quad (4)$$

$$f_2 = \frac{3(P^2 - 1)}{2(P^3 - 1)} \quad (5)$$

$$P = p_i/p_o \quad (6)$$

where  $p_i$  and  $p_o$  are the column inlet and outlet pressures. Large errors in the  $D_{go}$  value (diffusion in the gas phase at the outlet pressure) make all other calculations within the HETP equation erroneous [12].

Some methods for empirically assessing correct  $D_g$  values have been described (e.g., refs. 15-17). All such methods are combined with errors, depending on the fact that the instruments used for measuring diffusion themselves add errors owing to their interferences with the diffusion process. Theoretically, it is possible to derive a  $D_{go}$  value from eqn. 1 by using a capillary column with no stationary phase present. Ideally, this would give a non-retained peak from which it would be possible to calculate the HETP value. This method was described by several workers in the early 1960s [15,18,19], not taking into account the pressure drop over the column or any other retention mechanisms. If the  $f$  factors are included, the calculations still become straightforward. Assuming  $k' = 0$ ,  $C_l = 0$  and  $C_i = 0$  in eqn. 1 gives:

$$H = 2D_{go}f_1/v_o + C_{go}f_1v_o \quad (7)$$

where

$$C_{go} = \frac{r^2}{24D_{go}} \quad (8)$$

This yields

$$D_{go} = v_o/4 [H/f_1 \pm \sqrt{(H/f_1)^2 - r^2/3}] \quad (9)$$

where the positive root is used according to ref. 20. Replacing the outlet velocity in eqn. 9 by the mean velocity or elution time:

$$v_o = v/f_2 = L/(t_r f_2) \quad (10)$$

will give

$$D_{go} = L/(4t_r f_2) [H/f_1 + \sqrt{(H/f_1)^2 - r^2/3}] \quad (11)$$

$H$  is determined according to

$$H = L/N = B^2/(8 \ln 2t_r^2) \quad (12)$$

where  $L$  is the tube length,  $B$  is the peak width at half-height,  $N$  is the number of theoretical plates and  $t_r$  is the retention time. This means that it is possible to calculate a  $D_g$  value based on a chromatogram of a compound eluted from a column without stationary phase and corrected for the pressure drop over the column ( $f$  factors). Measuring diffusion coefficients by gas chromatography was reviewed in 1975 [21].

Unfortunately, the general theory is not as simple as that for determining a correct  $D_g$  value. In practice a small compound- and  $v_o$ -dependent adsorption/non-laminar flow term exists even when no stationary phase is present. This term will be referred to as  $C_a$ . Extra-column contributions will add a  $v_o^2$ -dependent term,  $D$ , described by Gaspar *et al.* [22]. Eqn. 7 thus becomes

$$H = 2D_{go}f_1/v_o + r^2f_1v_o/(24D_{go}) + C_a f_2 v_o + D(f_2 v_o)^2 \quad (13)$$

Solving  $D_{go}$  from this equation gives

$$D_{go} = v_o/4(K + \sqrt{K^2 - r^2/3}) \quad (14)$$

where

$$K = [H - C_a f_2 v_o - D(f_2 v_o)^2]/f_1 \quad (15)$$

and  $v_o$  can be replaced with  $v$  according to eqn. 10.

In this paper, three empirical methods to determine diffusion coefficients are discussed and compared with the FSG method [11].

## EXPERIMENTAL

The gas diffusion coefficients were obtained by headspace injections of the solutes into an empty, non-pretreated fused-silica tube of length 100 m and I.D. 0.32 mm (Quarts et Silice, Paris, France). The diffusion tube was installed in a Carlo Erba

(Milan, Italy) 4160 gas chromatograph. Hydrogen was used as the carrier gas and the inlet pressure was measured by a digital pressure gauge (Chrompack, Middelburg, The Netherlands). The inlet pressure ranged from 2.23 to 1.12 atm (outlet pressure = 1 atm), giving outlet velocities from 0.60 to 0.02 m/s.

Headspace samples (7  $\mu$ l) were injected in the split mode by use of a 10- $\mu$ l Hamilton syringe equipped with a 7-cm needle. The splitting ratio was maintained at 1:500 and the injector temperature was held at the same temperature as the oven, *i.e.*, 125°C. A flame ionization detector was used.

Four solutes were investigated, *n*-butane, *n*-hexane, *n*-dodecane and toluene. Signal recording and data handling were performed with an ELDS 900 laboratory data system (Chromatography Data Systems, Kungshög, Stenhamra, Sweden). The sampling rate was 18.2 s<sup>-1</sup>, giving 40–400 data points per peak.

Double or triple injections were performed at each new inlet pressure, giving a total of approximately 80 peaks per compound to be used for further calculations.

## RESULTS AND DISCUSSION

If eqn. 7 was true in the case of an open-tubular column with no stationary phase, a plot of  $D_{go}$  versus  $v_0$  according to eqn. 11 should generate a horizontal line. If any other relationship is registered, with a slope differing significantly from zero, this would imply that it was necessary to introduce some other term in eqn. 7. Such a term could be due to retention, caused by the fused-silica surface (*e.g.*, adsorption), to physical retention from gaseous friction on the column wall which could be called interfacial resistance or to extra-column effects (such as peak broadening in the injector or detector and time constants of the electronic recording system).

Indeed, a plot of  $D_{go}$ , calculated according to eqn. 11, yields a non-constant value. In Fig. 1 (marked  $\square$ ),  $D_{go}$  is plotted versus  $v_0$  for four compounds. The fact that the diffusion coefficient increases with increasing gas velocity indicates that an additional retention effect (or an extra-column effect) exists. This effect was discussed theoretically by Giddings and Seager in 1962 as "...non-uniform flow velocity existing over the tube crossing", but not applied experimentally [20]. In this work, extra-column effects were minimized by using a 100-m column with an inlet splitting ratio of *ca.* 1:500.

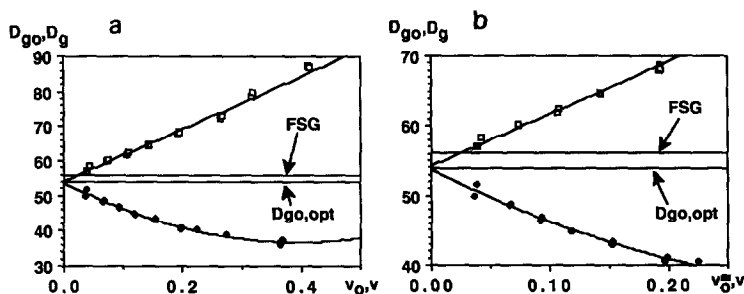


Fig. 1. (a) Diffusion coefficient of toluene at 125°C versus gas flow velocity:  $D_{go}$  versus  $v_0$  according to eqn. 11 ( $\square$ ),  $D_g$  versus  $v$  according to eqn. 16 ( $\blacklozenge$ ),  $D_{go,opt}$  according to eqn. 17 and FSG according to ref. 11. (b) Enlargement of part of (a).

TABLE I  
 $D_{go}$  VALUES OBTAINED BY DIFFERENT METHODS

Solute	Method <sup>a</sup>	$D_{go}$	$C_a$
<i>n</i> -Butane	Opt	63.59	0
	Opt	63.01	78.31
	Extrap1	63.60	—
	Extrap2	62.51	—
	FSG	63.70	—
<i>n</i> -Hexane	Opt	49.25	0
	Opt	49.14	31.13
	Extrap1	48.73	—
	Extrap2	50.16	—
	FSG	52.67	—
<i>n</i> -Dodecane	Opt	29.04	0
	Opt	28.72	87.72
	Extrap1	28.96	—
	Extrap2	27.80	—
	FSG	37.41	—
Toluene	Opt	54.02	0
	Opt	53.85	43.51
	Extrap1	54.23	—
	Extrap2	53.79	—
	FSG	56.05	—

<sup>a</sup> Opt = Optimized according to eqn. 17; Extrap1 = extrapolation to  $v_o=0$  from the plot of eqn. 9; Extrap2 = extrapolation to  $v_o=0$  from the plot of eqn. 16; FSG = calculated according to ref. 11.

The second method applied uses eqn. 11, but not taking into account the pressure drop over the column ( $f_1 = 1$  and  $f_2 = 1$ ). This is the method which has been used by many workers (e.g., refs. 20 and 23), preferably with short, wide-bore columns where the  $f$ -factors practically equal unity. The relationship becomes

$$D_g = L/(4t_r) [H + \sqrt{H^2 - (r^2/3)}] \quad (16)$$

where  $D_g$  is a mean binary diffusion coefficient and  $L/t_r$  equals the mean gas velocity in the column. This plot is also shown in Fig. 1 (marked  $\blacklozenge$ ). All curves tend to show a negative slope whereas earlier reported data on short, wide-bore columns generally yielded positive slopes [23]. Results from these methods are given in Table I.

Third, an optimization program was used by means of a least-squares fit of the measured values ( $H_i, v_{oi}$ ) to  $H = B_o/v_o + C_v_o + Dv_o^2$  according to

$$\min \sum_i [H_i - 2D_{go}f_1/v_{oi} + (r^2f_1/24D_{go} + C_af_2)v_{oi}]^2 \quad (17)$$

$D$  was set to zero in eqn. 17 according to the above discussion.  $D_{go}$  and  $C_a$  were optimized by linear programming, assuming that  $k'$  equals zero but taking into account the  $f$ -factors. The assumption that  $k'$  equals zero when a non-negligible  $C_a$  term is used is a contradictory but still reasonable simplification. Small  $k'$  values

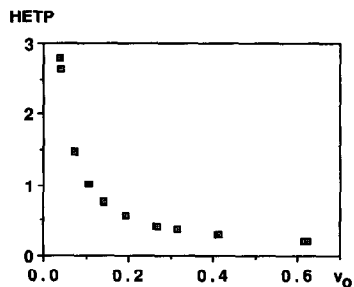


Fig. 2. HETP versus  $v_0$  for toluene at 125°C recorded on a non-coated open-tubular column (I.D. 0.32 mm).

(<0.05) are difficult to determine and the error introduced by this assumption is in the range of other errors (HETP calculations, etc.). The fit to the optimum function is given by the square root of the sum given in eqn. 17, divided by the number of observations:

$$\text{Error} = \sqrt{\sum (H_i - H_{\text{calc}})^2 / n} \quad (18)$$

In Table I, the calculated values of  $D_g$ , obtained using eqn. 17, for a number of compounds are shown. All measured values are on the low velocity side of the optimum  $v_0$  for minimum HETP (see Fig. 2). This also ensures that the correct sign is used in eqn. 9 for all calculations ( $v_0 < 4\sqrt{3} D_g/r$ ) [20]. When this extreme side of the HETP plot is used for optimization calculations, variations in the  $B$  term will have a very strong influence on the determination of a minimum in eqn. 17, whereas the influence of  $C_a$  is much weaker. In practice, an extra-column term, proportional to  $v_0^2$ , cannot be derived from these data owing to the small influence of such a term in the low velocity range. Table I also indicates that the existence of a  $C_a$  term alters the estimated  $D_g$  value by less than 1%.

As the fourth method, the FSG equation is applied to the calculation of  $D_g$  values [11]. These values are also listed in Table I.

Obviously, with the two methods where eqns. 11 and 16 are used for determining a  $D_g$  value, it is necessary to extrapolate to zero gas velocity in order to exclude all interfering processes. In this case, the  $f$ -factors are equal to unity, and  $D_{g0}$  in eqn. 11 should equal  $D_g$  in eqn. 16. The method for making this extrapolation is not straightforward if the curve form is unknown. The deviation from a constant value in the case of eqn. 11 is due to the approximation that  $k' = 0$  and  $C_a = 0$ . Neither of these parameters can easily be determined in these experiments. In Table I, an extrapolation based on a polynomial of the second-order in terms of  $v_0$  has been used. It is possible to show that this is a good assumption for small  $v_0$  values.

As expected, the  $D_g$  values calculated with any of the three methods are similar and have a lower limit than the values calculated from the FSG equation (Table I). Most empirical methods can be expected to yield higher values of the diffusion coefficient of a compound because the measurement itself influences (increases) the peak width for the observed compound. In a previous paper [12], especially the  $D_g$  values for  $n$ -alkanes were found to be significantly lower than the corresponding FSG values. However, the aromatic compound investigated in that study, biphenyl, showed

a much better agreement between observed values and those calculated from the FSG equation.

Table I and Fig. 1 show that the results obtained from the experimental methods are in good agreement, whereas those from the FSG method differ significantly, especially for larger molecules, *e.g.*, the deviation for *n*-butane is negligible, whereas the deviation for *n*-dodecane is as much as 37%. Obviously it is possible to estimate the  $D_g$  value by using a capillary column even if the pressure drop over the column is neglected. This can be done as long as an extrapolation back to zero gas velocity is made. When comparing the figures in Table I, it is also important to emphasize that all three experimentally applied methods use the same calculated HETP data, *i.e.*, accurate and carefully made calculations must be used in order not to introduce simultaneously systematic errors in all three methods.

Using this very limited set of data, no general correspondence can easily be observed between the deviation of FSG results from the experimental methods and the boiling points. The deviation for *n*-hexane (b.p. = 68.7°C) is in the same range as that for toluene (b.p. = 110.6°C).

## CONCLUSION

All three methods described seem to yield fairly acceptable values for the binary gas diffusion coefficients. The method described by eqn. 16 (marked by  $\blacklozenge$  in Fig. 1) is the simplest. This method can be applied accurately to an ordinary gas chromatographic system without the need to measure the pressure drop over the column. Extra-column effects must be minimized by using a long column in conjunction with a high splitting ratio.

The fact that the slope of the plot of  $D_g$  versus  $v_0$  differs significantly from zero cannot easily be attributed to one predominant property such as adsorption or extra-column effects in terms of time constants for the electronic recording system. Extensive calculations within this work have shown that the addition of a single term in the HETP equation, corresponding to adsorption (*i.e.*, proportional to  $v_0$ ) or corresponding to extra-column effects (*i.e.*, proportional to  $v_0^2$ ) also yields plots where  $D_g$  gives a slope versus  $v_0$ . Thus, in order to achieve accurate calculations of  $D_g$  by using eqn. 11 or 16, an extrapolation to zero gas velocity must be performed.

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