CHEMISTRY LETTERS, pp. 1081-1084, 1978. Published by the Chemical Society of Japan

KINETIC ELUCIDATION OF GAS CHROMATOGRAPHIC PEAKS OF LEADING AND TRAILING SHAPES

Koji TAKEUCHI and Tomihito KAMBARA
Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060

In general one observes a gas chromatographic peak of leading type at lower temperature and trailing shape at higher temperature. This fact is attributable to the slowness of vaporization and dissolution rate in the partition process. A mathematical treatment of the kinetics of nonequilibrium partition was developed and the theoretical prediction could clearly elucidate the asymmetric shapes observed at inadequate column temperatures.

The asymmetric shapes of gas chromatographic peaks, i.e., the trailing and leading types observed at higher and lower column temperatures, respectively, were experimentally confirmed.1) As to this fact, there has been given only a qualitative explanation that the partition isotherm of a solute component between the mobile and stationary phases is nonlinear, as described in several monographs.2-4) A mathematical model for nonlinear partition based on the numerical solution by means of computer was proposed.5) The theory by Schmauch6) explains only the leading type peak, and on the contrary the papers by the Littlewood school7,8) and others9,10) deal with only the trailing peak expressed as the convolution of exponential decay constant. The derivative method for gas chromatograph developed by Saitoh et al.11-16) is not only very useful in trace analysis but also gives important knowledges about the asymmetric shapes.

The system of differential equations17) expressing the changes of concentrations in the mobile and stationary phases with time was integrated and the outlet concentration in the mobile phase $C(\ell, \xi)$ is rounded into a Gaussian distribution shown by

$$C(\ell, \xi) = A \cdot G(\xi) \tag{1}$$

$$\xi = t - t_R \tag{2}$$

$$A = p_0 C_0 t_0 p_i^{-1} \tag{3}$$

$$G(\xi) = \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left(-\frac{\xi^2}{2\sigma^2}\right) \tag{4}$$

In these equations, ℓ is the column length, t time, t_R retention time, p_0 and

p_i the pressure at the outlet and inlet, C_0 the solute concentration injected with a time duration t_0, A the peak area and σ is the standard deviation of the Gaussian distribution $G(\xi)$. The change of the solute concentration in the stationary phase with time is shown by

$$F_s K \frac{\partial C_s}{\partial t} = -\alpha(C_s - KC) \tag{5}$$

where F_s is the fraction by volume of stationary phase, α and αK are the rate constants of dissolution and vaporization, respectively. At the appropriate temperature, both the rate constants of dissolution and vaporization being great, the term in the left-hand side of eqn. 5 is negligibly small compared with two terms in the right-hand side. Then, one has the partition coefficient:

$$K = \frac{C_s}{C} = \frac{C_s(\ell,\ \xi)}{C(\ell,\ \xi)} \tag{6}$$

At lower temperature, however, the solute equilibration does not hold, since the rate of vaporization is slow. In this case the major part of solute exists in the stationary phase and eqn. 5 is transformed into the ordinary differential equation concerning the stationary phase concentration.

$$\frac{d}{d\xi} C_s(\ell,\ \xi) + \frac{1}{z} C_s(\ell,\ \xi) = \frac{AK}{z} G(\xi) \tag{7}$$

with

$$z = F_s K \alpha^{-1} \tag{8}$$

With the boundary condition shown by

$$C_s(\ell,\ \xi) = 0 \quad \text{for} \quad \xi = \pm\infty \tag{9}$$

one derives

$$C(\ell,\ \xi) = \frac{A}{z} \exp\left(-\frac{\xi}{z}\right) \int_0^{\xi} G(x) \exp\left(\frac{x}{z}\right) dx \tag{10}$$

Such an expression is found in the book by Littlewood,18) however, it has remained undeveloped. Upon applying the integration by parts successively one derives

$$\int_0^{\xi} G(x) \exp\left(\frac{x}{z}\right) dx = z \exp\left(\frac{\xi}{z}\right) \cdot \left\{ G - z G^{(1)} + z^2 G^{(2)} - z^3 G^{(3)} + \cdots \right\} \tag{11}$$

Thus, the outlet concentration is given by

$$C(\ell,\ \xi) = A\left(G - z G^{(1)} + z^2 G^{(2)} - z^3 G^{(3)} + \cdots\right) \tag{12}$$

Eqn. 12 represents the leading peak, as shown in Fig. 1.

On the other hand, at higher temperature the solute mainly exists in the mobile phase, and eqn. 5 is transformed by means of eqns. 4 and 6 into the ordinary differential equation concerning the mobile phase concentration given by

$$\frac{d}{d\xi} C(\ell, \xi) - \frac{1}{z} C(\ell, \xi) = - \frac{A}{z} G(\xi) \tag{13}$$

Integration of this equation yields

$$C(\ell, \xi) = A(G + zG^{(1)} + z^{2}G^{(2)} + z^{3}G^{(3)} + \cdots) \tag{14}$$

As shown in Fig. 1, this expression shows the trailing peak. It should be emphasized that eqns. 12 and 14 can also be derived by the successive insertion of

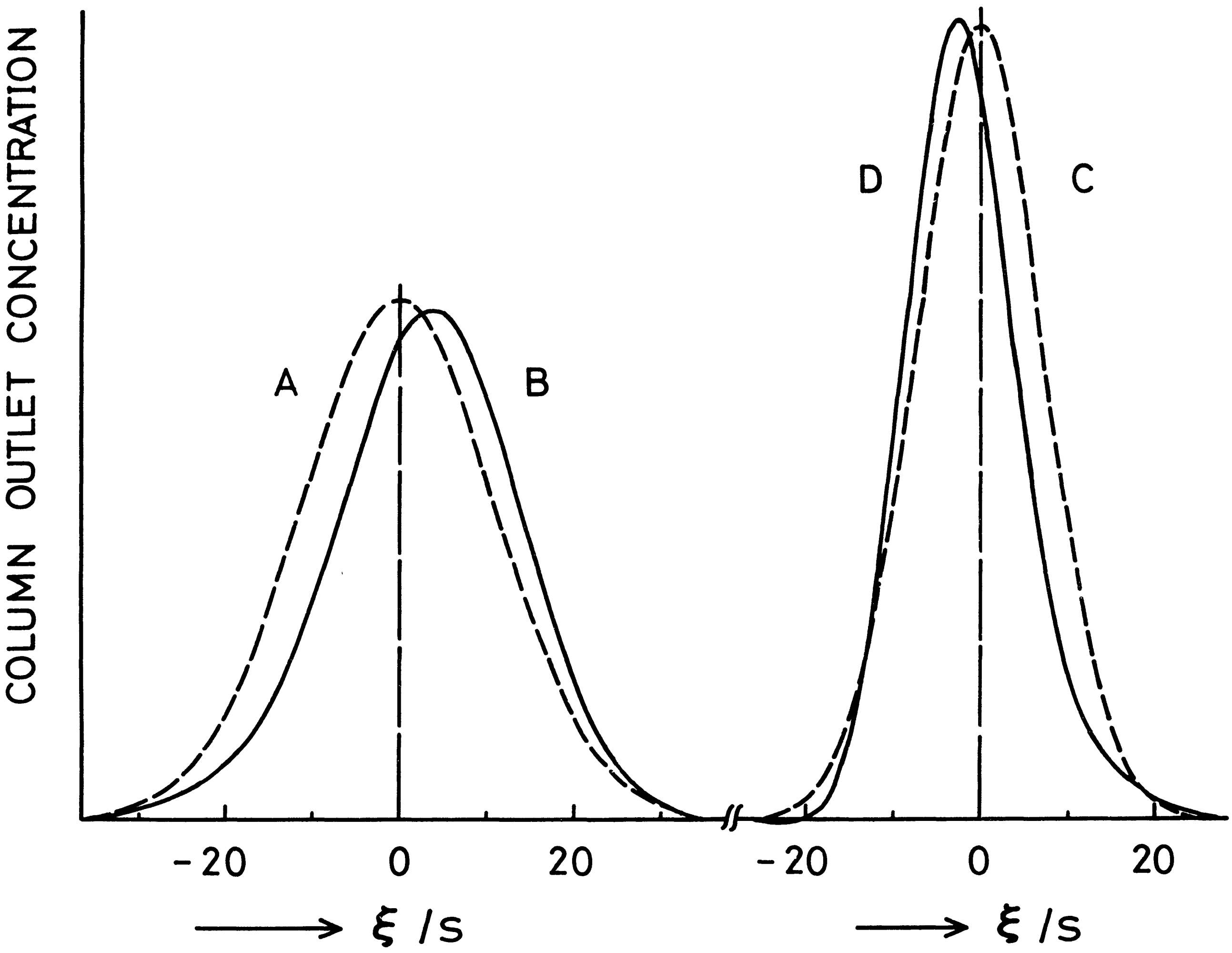

Fig. 1. Theoretical elution profiles calculated with the following values. Curve A, $z = 0$, $\sigma = 11.1$; curve B, $z = 4.44$, $\sigma = 11.1$; curve C, $z = 0$, $\sigma = 7.25$; curve D, $z = 3.26$, $\sigma = 7.25$ s.
The Gaussian distribution shown by dashed lines (curves A and C) corresponds to $z = 0$. Curves B and D show the leading and trailing peaks calculated by eqns. 12 and 14, respectively.

eqns. 4 and 6 into eqns. 7 and 13. It is now concluded that the asymmetric gas chromatographic peaks are expressed by the series consisting of the Gaussian distribution $G(\xi)$ and its derivatives $G^{(n)}$. Integration of eqns. 12 and 14 with respect to ξ in the interval from $-\infty$ to $+\infty$ yields A, representing the law of conservation of mass.

The theoretical elution profiles calculated including the derivatives until fifth order by means of eqns. 12 and 14, showing the peaks of leading and trailing type, respectively, are reproduced in Fig. 1. When the value Σ was smaller than 0.45σ, eqns. 12 and 14 was found to fit well. A symmetric Gaussian peak is obtained when $\sigma = 0$, and the distortion of peak becomes more remarkable with increasing value of Σ. The mathematical analysis of the experimentally observed gas chromatograms of asymmetric shapes has been carried out successfully by the aid of the familiar curve fitting method. The results will be published in the near future.

Thanks are due to Dr. Kunio Ohzeki for his kind discussions.

REFERENCES AND NOTE

1) T. Kambara and H. Kodama, J. Chromatogr., 17, 66 (1965).
2) A. B. Littlewood, "Gas Chromatography", Academic Press, London (1962), p. 12.
3) H. Purnell, "Gas Chromatography", John Wiley & Sons, New York (1962), p. 82.
4) A. I. M. Keulemans, in C. G. Verver (Editor), "Gas Chroamtography", 2nd ed., Reinhold, New York (1959), Chapt. 4.
5) J. E. Funk and G. Houghton, Nature, 188, 389 (1960).
6) L. J. Schmauch, Anal. Chem., 31, 225 (1959).
7) A. H. Anderson, T. C. Gibb and A. B. Littlewood, Anal. Chem., 42, 434 (1970).
8) A. H. Anderson, T. C. Gibb and A. B. Littlewood, J. Chromatogr. Sci., 8, 640 (1970).
9) W. W. Yau, Anal. Chem., 49, 395 (1977).
10) R. E. Pauls and L. B. Rogers, Anal. Chem., 49, 625 (1977).
11) T. Kambara, K. Saitoh and K. Ohzeki, Bunseki Kagaku, 15, 517 (1966).
12) T. Kambara, K. Saitoh and K. Ohzeki, Anal. Chem., 39, 409 (1967).
13) T. Kambara and K. Saitoh, J. Chromatogr., 35, 318 (1968).
14) T. Kambara, K. Saitoh and K. Ohzeki, Bunseki Kagaku, 16, 721 (1967).
15) T. Kambara, S. Katada and K. Saitoh, Bunseki Kagaku, 18, 1225 (1969).
16) K. Saitoh and T. Kambara, Kagaku no Ryoiki, 23, 11 (1969).
17) T. Kambara and K. Ohzeki, J. Chromatogr., 21, 383 (1966).
18) Reference 2, p. 166, eqns. 5.55 and 5.56.

* To whom all correspondences should be addressed.

(Received July 29, 1978)