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RETENTION VOLUME IN HIGH-PRESSURE GAS CHROMATOGRAPHY

I. THERMODYNAMICS OF THE SPECIFIC RETENTION VOLUME

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SUMMARY

Formal thermodynamic relationships were derived for the specific retention volume of the solute in the solute–carrier gas–stationary liquid ternary system, applicable at higher pressures and with a negligible pressure drop across the column. Special attention has been paid to the effects of the solubility of the carrier gas in the stationary phase and to the non-ideal behaviour of the carrier gas. The relationships derived show that the pressure dependence of the specific retention volume alone can give only approximate information on binary solute–carrier gas systems. If more precise data are to be obtained, it is necessary to know additional parameters (the partial molar volume of solute in the solute–carrier gas–stationary liquid ternary system, activity coefficients of the dissolved carrier gas and their dependence on the composition, and the molar fraction of dissolved carrier gas), which cannot be obtained reliably from chromatographic data.

INTRODUCTION

Originally, the carrier gas was assumed to play a largely passive role in gas chromatography: it was considered merely as a means of transporting the solute from one end of the column to the other. This concept, which is applicable to a perfect gas, is incorrect under currently used chromatographic conditions and fails completely at higher pressures. In fact, the carrier gas always takes a more or less active part in the equilibration of the solute between the gaseous and the stationary phases. This more precise understanding of the role of the carrier gas was discussed by Everett and Stoddart[1] in 1961 and was utilized in the separation of porphyrins by Klesper *et al.*[2] in 1962. Since then, a number of papers have been published in which the non-ideality of the carrier gas was utilized in separations. Examples are the series of papers by Sie and co-workers[3–8] and by Giddings and co-workers[9–13].

Simultaneously with the practical utilization of the equilibrium shifts induced by the non-ideality of the carrier gas, methods began to be sought in order to use the simplicity of the chromatographic technique for obtaining thermodynamic data that characterize separations. The idea of using a gas chromatograph to obtain data on the thermodynamic properties of the solute–carrier gas–stationary liquid system is not new: Young's review[14] can be referred to in this context. Whereas the data referred to the stationary phase, such as the activity coefficient of the solute and its temperature dependence, have only limited practical utility owing to the special character of the chromatographic system, the information on binary gaseous mixtures of the type vapour of organic liquid–permanent gas has a more universal applicability and can be of wider interest[15].

The possibility of employing the pressure dependence of retention data for obtaining the second cross-virial coefficient of the solute–carrier gas mixture, originally suggested by Everett and Stoddart[1], was later utilized more extensively by Desty *et al.*[16] and particularly by Cruickshank and co-workers[17–20]. The measurements were performed within relatively narrow limits of mean pressures (within about 1–10 atm), which has the inherent disadvantages that, in addition to relatively high demands on the precision of the measured data, problems associated with the pressure drop across the column are encountered. If the pressure drop reaches values that are comparable in order of magnitude with the absolute pressure in the column, it is necessary to carry out relatively complicated averaging of the pressure-dependent components of the capacity ratio by applying averaging integrals. With gases that show ideal behaviour, these integrals have been expressed in an analytical form by Everett[21] and are known as the J_n^m factors.

A substantially more involved situation occurs if it is necessary to consider the real behaviour of the carrier gas. Explicit expressions for the pressure dependence of the capacity ratio have to be found in order to carry out corrections for the compressibility of the mobile phase. However, the functions that form the above expressions are usually transcendent with respect to pressure and can be expressed explicitly only by making significant simplifications. This applies particularly to the fugacity coefficient of the solute in the gaseous phase and for the correction of the capacity ratio for the solubility of the carrier gas in the stationary phase.

Both of the above disadvantages can be avoided by providing for the eluent expansion to occur outside the column. In this case, the column operates under virtually isobaric conditions, the pressure drop between the column inlet and the detector being determined by a throttling device independent of the column. Such a modification makes it possible to increase the pressure range of the measurements and to decrease the demands on the precision of the data measured. The isobaric model of the chromatographic column, corresponding to the above experimental arrangement, is much simpler than models that involve the pressure drop across the column. On the other hand, operation under higher pressures leads to greater demands on the strictness of the thermodynamic processing of the experimental results.

Above all, it is necessary to take into account the role of the carrier gas dissolved in the stationary phase, as the solubility of the carrier gas can reach very significant levels under higher pressures[3]. Further, a more precise calculation of the fugacity coefficient of the solute in the gaseous phase is necessary. Finally, in chromatography with the carrier gas in a state close to the critical point, more general problems are encountered associated with comparing the system in the column with a reference system, which is usually placed in a region of low pressures. In this paper, mainly the first two problems are dealt with in greater detail.

SPECIFIC RETENTION VOLUME

The classical thermodynamics of the chromatographic partition coefficient[1] are based on the assumption of a binary character of both phases. The vapour of the stationary liquid present in the gaseous phase and the concentration of the carrier gas dissolved in the stationary liquid are neglected.

The solute capacity ratio, k_1, which determines the chromatographic retention, can be defined as the equilibrium ratio of the number of moles in the liquid (stationary) phase to that in the gaseous (mobile) phase within an element of the column of unit volume. Hence,

$$k_1 = \left[\frac{n_1^{\mathrm{L}}}{n_1^{\mathrm{G}}}\right]_{\mathrm{equil.}} = \left[\frac{x_1}{y_1}\right]_{\mathrm{equil.}} \cdot \frac{\Sigma n^{\mathrm{L}}}{\Sigma n^{\mathrm{G}}} = \kappa_1 \cdot \frac{\Sigma n^{\mathrm{L}}}{\Sigma n^{\mathrm{G}}} \tag{1}$$

In this discussion, the quantities referring to the solute, carrier gas and stationary phase are designated by the subscripts 1, 2 and 3, respectively, and the superscripts G and L are used in order to distinguish between quantities concerning the gaseous and the liquid (stationary) phase, respectively. Thus, n_1^{L} and n_1^{G} are the number of moles of solute in the stationary and in the gaseous phase in a unit-volume element of the column, Σn^{L} and Σn^{G} are the sums of the number of moles of solute, carrier gas and sorbent material in the liquid and in the gaseous phase, respectively, in a unit-volume element of the column, and x_1 and y_1 are the molar fractions of the solute in the liquid and in the gaseous phase, respectively.

Provided that (i) the solute concentrations in both phases are negligible, (ii) the stationary liquid is non-volatile and (iii) the carrier gas is insoluble in the stationary liquid, then $\Sigma n^{\mathrm{L}} \approx n_3^{\mathrm{L}}$ and $\Sigma n^{\mathrm{G}} \approx n_2^{\mathrm{G}}$, and

$$k_1 = \frac{n_3^{\mathrm{L}}}{n_2^{\mathrm{G}}} \cdot \kappa_1 \tag{2}$$

There is a simple relationship between the partition coefficient, κ_1, and the specific retention volume of the solute if the pressure drop across the column can be neglected, *i.e.*, if $P_i \approx P_o = \bar{P}$, $u_i \approx u_o = \bar{u}$ and $v_i \approx v_o = \bar{v}$, where P_i and P_o are the absolute inlet and outlet column pressures, $\bar{P}$ is the absolute mean column pressure, u_i and u_o are the forward flow velocities of the mobile phase at the inlet and outlet of the column (at pressures P_i and P_o) and at the column temperature T, $\bar{u}$ is the forward flow velocity of the mobile phase as measured at the column temperature T and the mean pressure $\bar{P}$, v_i and v_o are the volume flow-rates at the inlet and outlet of the column (at pressures P_i and P_o) and at the column temperature T, and $\bar{v}$ is the volume flow-rate of the mobile phase in the column at column temperature T and mean pressure $\bar{P}$. The retention time, t_{R1}, of the solute with a capacity ratio k_1 is then given by

$$t_{R1} = (1 + k_1) \cdot \frac{l}{\bar{u}} \tag{3}$$

where l is the column length.

Let us define the specific retention volume, V_g^{Tr}, as the volume of the mobile phase necessary to elute the solute throughout the column, reduced by the column void volume, expressed at the mean column pressure $\bar{P}$ and at an arbitrarily chosen reference temperature Tr, and referred to 1 g of the stationary liquid in the column. Thus,

$$V_g^{Tr} = \frac{\bar{v}\, z_2^{Tr}(\bar{P}, Tr)\, Tr}{w_3\, z_2(\bar{P}, T)\, T} \cdot (t_{R1} - t_m) \tag{4}$$

where z_2^{Tr} is the compressibility factor of the carrier gas at pressure $\bar{P}$ and temperature Tr, z_2 is the compressibility factor of the carrier gas at pressure $\bar{P}$ and column temperature T, w_3 is the weight of the stationary liquid contained in the column and t_m is the dead retention time ($l/\bar{u}$).

The above definition of the specific retention volume differs from the conventional definition merely by the arbitrariness in the choice of the reference temperature: in the classical definition, $Tr = 273.2$ °K. The usefulness of this modification in high-pressure gas chromatography is apparent from the following simple consideration. If $T > T_c > Tr$ and $\bar{P} > P_c$, then the mobile phase in the column is formed by a compressed gas above its critical temperature. However, if the gas is cooled to the temperature Tr at a pressure $\bar{P} > P_c$ according to the classical definition, it will liquefy, and discontinuities will occur on the V_g^{Tr} *versus* $\bar{P}$ curves. It is therefore reasonable to provide for the choice of $Tr > T_c$, which is just the purpose of the above modification.

The substitution of eqns. 3 and 2 into eqn. 4 results in

$$V_g^{Tr} = \frac{z_2^{Tr}\, R\, Tr}{M_3} \cdot \frac{\kappa_1}{\bar{P}} \tag{5}$$

where M_3 is the molecular weight of the stationary liquid and R is the gas constant. The applicability of eqn. 5 is qualified by the validity of the assumptions made in its derivation. When disregarding the difference between the measured peak maximum and the ideal retention time[22-23] and neglecting, at absolute pressures reaching several tens of an atmosphere, pressure drops that do not exceed a few tenths of an atmosphere, only the classical assumptions (i), (ii) and (iii) remain to be considered. Owing to the sensitivity of ionization detectors, the assumption of infinite dilution of the solute in both phases can almost always be practically fulfilled. Similarly, the effect of the volatility of the stationary liquid can be eliminated by a suitable choice of both the stationary liquid and the working temperature.

However, the situation with solubility of the carrier gas in the stationary phase is different, as this solubility can affect the solute retention more significantly. If the carrier gas dissolves in the stationary liquid, then $\Sigma n^L \approx n_3^L + n_2^L$.

The solubility of the carrier gas in the stationary liquid can be described by means of the respective partition coefficient:

$$\kappa_2 = \left[\frac{x_2}{y_2}\right]_{\text{equil.}} \approx x_2 = \frac{n_2^L}{n_3^L + n_2^L} \tag{6}$$

In accordance with the assumption of infinite dilution of the solute in the gaseous phase, the molar fraction of the carrier gas, y_2, in the latter is considered to be approximately unity. Thus, the expression for k_1, analogous to eqn. 2, will acquire the form

$$k_1^+ = \frac{n_3^L}{n_2^G} \cdot \kappa_1^+ \cdot \frac{1}{1 - \kappa_2} \tag{7}$$

It follows from the above discussion that the carrier gas dissolved in the liquid phase influences the retention in two ways: it increases the number of moles of the liquid phase per unit volume of the column and, at the same time, it modifies the sorption properties of the liquid phase. The increase in the capacity ratio due to the increase in the amount of liquid phase in the column is characterized by the factor $1/(1 - \kappa_2)$; the altered properties of the liquid phase are, for the time being, indicated by a + as a superscript to the respective symbols. In the following text, this superscript will be generally used to denote the composition-dependent quantities that refer to the ternary solute–carrier gas–stationary phase system.

PARTITION COEFFICIENTS κ^+ AND κ_2

Let us start from the Gibbsian condition of equilibrium: at equilibrium, the fugacities of the solute in both phases are the same, and the equation

$$\varphi_1(T, \bar{P}, y)\, y_1 \bar{P} = \gamma_1^+(T, \bar{P}, x)\, x_1 f_1^0(T, \bar{P}) \tag{8}$$

holds, from which it follows that

$$\frac{\kappa_1^+}{\bar{P}} = \frac{x_1}{\bar{P} y_1} = \frac{\varphi_1(T, \bar{P}, y)}{\gamma_1^+(T, \bar{P}, x) \cdot f_1^0(T, \bar{P})} \tag{9}$$

where φ_1 is the solute fugacity coefficient in the solute–carrier gas mixture at temperature T and mean column pressure $\bar{P}$, γ_1^+ is the activity coefficient of the solute in the ternary system solute–carrier gas–stationary phase at T and $\bar{P}$ and f_1^0 is the fugacity of the pure liquid solute at T and $\bar{P}$.

The pressure dependence of the product $\gamma_1^+ f_1^0$ can formally be eliminated by introducing activity coefficients at a reference pressure[24] by means of the thermodynamically rigorous relationship:

$$\gamma_1^+ f_1^0 = \gamma_1^{+Pr}(T, Pr, x)\, f_1^{0Pr}(T, Pr) \exp\left[\int_{Pr}^{\bar{P}} \frac{\overline{V}_1^{L+}(T, P, x)}{RT} \cdot \mathrm{d}P\right] \tag{10}$$

where γ_1^{+Pr} is the activity coefficient of the solute at temperature T, an arbitrary reference pressure Pr and a constant liquid phase composition equal to that at pressure $\bar{P}$, f_1^{0Pr} is the fugacity of the pure solute at temperature T and reference pressure Pr and $\overline{V}_1^{L+}$ is the partial molar volume of the solute in the liquid phase at temperature T and at a constant liquid phase composition equal to that at pressure $\bar{P}$. A basic condition for the validity of eqn. 10 is the preservation of an invariable composition of the liquid phase when passing from pressure $\bar{P}$ to the reference pressure Pr.

This condition cannot be fulfilled precisely in our case, as the solubility of the carrier gas in the stationary phase varies with the pressure and the liquid phase composition varies accordingly. In spite of the above reservation, eqn. 10 represents the only acceptable means of providing for at least an approximate application of the isothermal–isobaric integrals of the Gibbs–Duhem equation to the concentration dependence of the activity coefficient of the solute. Employing eqn. 10, eqn. 9 can be rewritten as

$$\frac{\kappa_1^{+}}{\bar{P}} = \frac{\varphi_1 \exp\left[\int_{Pr}^{P} -(\bar{V}_1^{L+}/RT)\,\mathrm{d}P\right]}{\gamma_1^{+Pr} f_1^{0Pr}} \tag{11}$$

The partition coefficients of the carrier gas, κ_2, can be derived from a relationship analogous to eqn. 8. The equation

$$\varphi_2^0(T, \bar{P})\,\bar{P} = \gamma_2^*(T, \bar{P}, x)\, x_2\, H_2(T, \bar{P}) \tag{12}$$

holds, from which

$$\kappa_2 = \frac{\varphi_2^0 \bar{P}}{\gamma_2^* H_2} \tag{13}$$

where φ_2^0 is the fugacity coefficient of the pure carrier gas at temperature T and pressure $\bar{P}$, γ_2^* is the activity coefficient of the carrier gas dissolved in the liquid phase at T and $\bar{P}$, referred to an infinitely dilute solution as a reference state, and H_2 is the Henry law constant of the carrier gas in the stationary phase at T and $\bar{P}$.

In deriving eqn. 13, both phases have been considered to be infinitely dilute solutions of the solute. Hence the effects of the solute on the fugacity of the carrier gas (Lewis–Randall rule) and on the solubility of the carrier gas in the stationary phase have been neglected.

Through a formal application of eqn. 10, the product $\gamma_2^* H_2$ in eqn. 13 can further be rearranged, so that

$$\kappa_2 = \frac{\varphi_2^0 \bar{P} \exp\left[\int_{Pr}^{P} -(\bar{V}_2^{L}/RT)\,\mathrm{d}P\right]}{\gamma_2^{*Pr}(T, Pr, x)\, H_2^{Pr}(T, Pr)} \tag{14}$$

where γ_2^{*Pr} is the activity coefficient of the carrier gas dissolved in the liquid phase at temperature T and reference pressure Pr and at a constant liquid phase composition equal to that at pressure $\bar{P}$, referred to an infinitely dilute solution reference state. H_2^{Pr} is the Henry law constant of the carrier gas in the pure liquid phase at temperature T and reference pressure Pr and $\bar{V}_2^{L}$ is the partial molar volume of the carrier gas dissolved in the pure liquid phase at temperature T and a constant liquid phase composition equal to that at pressure $\bar{P}$. The same reservations hold for the transition from eqn. 13 to eqn. 14 as those specified for the transition from eqn. 9 to eqn. 11.

Finally, when replacing the expression $\kappa_1/\bar{P}$, applicable to a binary system, by $\kappa_1^{+}/[\bar{P}(1-\kappa_2)]$, valid for the ternary system, in eqn. 5, a relationship that is sufficiently general for our purposes is obtained:

$$V_g^{Tr} = \frac{z_2^{Tr}\,RTr}{M_3}\cdot\frac{\varphi_1 \exp\left[\int_{Pr}^{\bar{P}} -(\overline{V}_1^{L+}/RT)\,\mathrm{d}P\right]}{\gamma_1^{+Pr} f_1^{0Pr}}\cdot\frac{\gamma_2^{*Pr} H_2^{Pr}}{\gamma_2^{*Pr} H_2^{Pr} - \varphi_2^0 \bar{P} \exp\left[\int_{Pr}^{\bar{P}} -(\overline{V}_2^{L}/RT)\,\mathrm{d}P\right]} \tag{15}$$

LIQUID PHASE

Dependence of the activity coefficients on the composition

The properties of the liquid phase affect the specific retention volume by means of the functions $\gamma_1^{+Pr} f_1^{0Pr}$ and $\gamma_2^{*Pr} H_2^{Pr}$, generally f_i^{LPr}/x_i, where $f_i^{LPr}(T,Pr,x)$ is the fugacity of the ith component of the liquid phase at a reference pressure Pr, temperature T and a given composition of the liquid phase, and by means of the functions $\overline{V}_1^{L+}$ and $\overline{V}_2^{L}$. At a constant temperature, the functions f_i^{LPr} are dependent only on the composition of the liquid phase and comply with the isothermal–isobaric Gibbs–Duhem equations.

Krichevskii[25] derived the following relationships for dilute regular ternary solutions:

$$\left.\begin{aligned}
RT\ln f_1^{LPr} &= RT\ln H_1^{Pr}x_1 - a_{13}(1-x_3^2) + a_{12}x_2^2 + (a_{12}+a_{13}-a_{23})\,x_2x_3\\
RT\ln f_2^{LPr} &= RT\ln H_2^{Pr}x_2 - a_{23}(1-x_3^2) + a_{12}x_1^2 + (a_{12}+a_{23}-a_{13})\,x_1x_3\\
RT\ln f_3^{LPr} &= RT\ln f_3^{0Pr}x_3 + a_{23}x_2^2 + a_{13}x_1^2 + (a_{13}+a_{23}-a_{12})\,x_1x_2
\end{aligned}\right\} \tag{16}$$

where H_1^{Pr} is the Henry law constant in the binary solute–stationary phase system at temperature T and reference pressure Pr, f_3^{0Pr} is the fugacity of the pure stationary liquid at temperature T and reference pressure Pr and a_{ij} are binary constants dependent only on T and Pr. System 16 is a simplified form of Margules' symmetrical equation of the third order for a ternary system (see ref. 26).

In our case of an infinitely dilute solution of the solute, $x_1 \to 0$ and $x_3 \to 1 - x_2$, and

$$\ln f_1^{LPr} = \ln H_1^{Pr}x_1 + \frac{a_{12}-a_{13}-a_{23}}{RT}\cdot x_2 + \frac{a_{23}}{RT}\,x_2^2 \tag{17}$$

$$\ln f_2^{LPr} = \ln H_2^{Pr}x_2 - \frac{a_{23}}{RT}\cdot(2x_2 - x_2^2) \tag{18}$$

from which it follows that

$$\gamma_1^{+Pr} f_1^{0Pr} = \gamma_1^{*+Pr} H_1^{Pr} = \frac{f_1^{LPr}}{x_1} = H_1^{Pr}\exp[(\alpha-\beta)\,x_2 + \beta\,x_2^2] \tag{19}$$

$$\gamma_2^{*Pr} H_2^{Pr} = \frac{f_2^{L,Pr}}{x_2} = H_2^{Pr} \exp[-\beta(2x_2 - x_2^2)] \tag{20}$$

where γ_1^{*Pr} is the activity coefficient of the solute in the ternary solute–carrier gas–stationary phase system, referred to the reference state of an infinitely dilute solution of the solute in the stationary phase, $\alpha = (a_{12} - a_{13})/RT$, and $\beta = a_{23}/RT$.

Eqns. 19 and 20 express the required dependences of the activity coefficients of the solute and carrier gas on the liquid phase composition. If $(\alpha - \beta)x_2 \gg \beta x_2^2$ and $2x_2 \gg x_2^2$ for a carrier gas with a low solubility, the concentration dependence of the activity coefficients can be further simplified:

$$\gamma_1^{*Pr} \approx 1 + (\alpha - \beta)x_2 \tag{21}$$

$$\gamma_2^{*Pr} \approx 1 - 2\beta x_2 \tag{22}$$

In a general case, however, the relatively simple system 16 may become unsatisfactory and more complicated integrals will have to be used. A survey of the expansions of the dependences of activity coefficients on concentration, based on the general Wohl expansion for a ternary system, was given by Hála *et al.*[26], for example.

Partial molar volumes of the components in the liquid phase

The partial molar volume of the solute in the liquid phase and also its pressure dependence are closely associated with the problem mentioned in the introduction, namely the comparison of two liquid systems, one in the column at pressure $\bar{P}$ and the other, a reference system, considered at the same temperature and composition, but at a very low reference pressure *Pr*.

For regions close to saturation, approximate methods for calculating the partial molar volumes from an equation of state, based on the theorem of corresponding states and empirical rules of mixing the constants of pure substances[27], have been developed. However, owing to the special nature of stationary liquids employed in chromatography, the above rules are of no use for our purposes. Direct experimental data, especially for ternary systems, do not exist.

When neglecting, at least in a region far from the critical region of the mixture, the pressure dependence of the partial molar volumes of the components in the condensed phase, the equation

$$\int_{Pr}^{\bar{P}} \frac{\bar{V}_i^{L+}}{RT} \cdot \mathrm{d}P = \frac{\bar{V}_i^{L+}}{RT} \cdot (\bar{P} - Pr) \tag{23}$$

holds approximately and the problem is reduced to seeking the pseudo-constant $\bar{V}_i^{L+}$ at a given composition of the liquid phase and at a given temperature. The replacement of the quantity $\bar{V}_i^{L+}(T,x)$ by the molar volume of the pure component in the liquid phase at the temperature T, $V_i^{0L}(T)$ (refs. 16 and 21), is not a very satisfactory solution as the actual solutions of both the solute and dissolved carrier gas correspond to opposite sides of the concentration range. In addition, further problems are encountered, for example those in determining the molar volume of the liquefied carrier gas above its critical temperature.

With the solute, the independent determination of the partial molar volume in an infinitely dilute solute–stationary phase binary system, *i.e.*, the interchange of $\bar{V}_1^{L\infty}$ and $\bar{V}_1^{L}$, can be considered to be an adequate approach. With the carrier gas, the partial molar volume, $\bar{V}_2^{L}$, can be determined from the pressure dependence of the solubility of the carrier gas in the pure stationary liquid. However, at pressures and temperatures near the critical region, the assumption of the independence of the partial molar volumes of the components in the condensed phase on pressure is no longer valid. On the contrary, in this region significant changes in the partial molar volumes occur upon changing the state variables, and the value of eqn. 10 becomes very questionable in this case.

GASEOUS PHASE

Fugacity coefficient

The fugacity coefficient of a component of a gaseous mixture, $\varphi_i = f_i^G(T,P,y)/y_iP$, is connected with the equation of state of the gaseous mixture through the relationship

$$\ln \varphi_i = \frac{1}{RT} \int_{v_m}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,\,v,\,n_j} - \frac{RT}{v_m} \right] \mathrm{d}v_m - \ln z_m \tag{24}$$

where v_m is the volume of the gaseous mixture at temperature T and pressure P and z_m is the compressibility factor of the mixture at T and P.

The choice of a suitable equation of state, necessary for calculating the volume v_m of the mixture, compressibility factor z_m and the factor $\partial P/\partial n_i$, is determined by the precision required and the temperature range. In gas chromatography, the virial equation of state with the second or third coefficient is usually employed, from which it follows for the fugacity coefficient of the solute that

$$\ln \varphi_1 = \frac{2}{V_2^G} \cdot B_{12} + \frac{3}{2\,(V_2^G)^2} \cdot C_{122} - \ln z_2 \tag{25}$$

where V_2^G is the molar volume of the pure carrier gas at T and $\bar{P}$ and B_{12} and C_{122} are the cross-virial coefficients of the binary mixture of solute and carrier gas at temperature T. The molar volume and compressibility factor of the pure carrier gas at the column temperature T and mean pressure $\bar{P}$ have to be determined through the independent solution of the equation of state of the carrier gas.

In the low-pressure region, a simplification is sometimes introduced that consists in replacing the molar volume of the carrier gas by the molar volume of an ideal gas at the same temperature (T) and pressure ($\bar{P}$) in eqn. 25, *i.e.*,

$$\ln \varphi_2 = \frac{2\,B_{12}}{RT} \cdot \bar{P} + \frac{3}{2} \cdot \frac{C_{122}}{R^2T^2} \cdot \bar{P}^2 \tag{25a}$$

However, this simplification will be inapplicable at higher pressures, and the deviations from eqn. 25a found experimentally then leed to false conclusions about the necessity for adding further terms of virial expansion.

The virial equation terminated after the third term will be unsatisfactory for describing the properties of the gaseous phase close to the critical point of the carrier gas (Supercritical Fluid Chromatography). In this case, it is recommended that some of the semi-empirical equations of state should be used, such as the modified Redlich–Kwong equation (see ref. 28), rather than increasing the number of the terms of virial expansion.

DISCUSSION

Eqn. 15 can be written in a briefer form:

$$V_g^{Tr} = \frac{z_2^{Tr}\, RTr}{M_3} \cdot \frac{q_1 \exp\left[\int_{Pr}^{P} - (\bar{V}_1^{L+}/RT)\,\mathrm{d}P\right]}{H_1^{Pr}} \cdot \frac{1}{\gamma_1^{+*Pr}(1 - x_2)} \tag{26}$$

or, after substituting into this equation from eqns. 19, 23 and 25 and introducing the approximation $\bar{P} - Pr \approx \bar{P}$,

$$\frac{z_2}{z_2^{Tr}} \cdot V_g^{Tr} = \frac{RTr}{M_3\, H_1^{Pr}} \cdot \exp\left[\frac{2(B_{12}/z_2) - \bar{V}_1^{L+}}{RT} \cdot \bar{P} + \frac{3\, C_{122}}{2\, z_2^2\, R^2\, T^2} \cdot \bar{P}^2\right] \cdot \frac{\exp - [(\alpha - \beta)\, x_2 + \beta\, x_2^2]}{1 - x_2} \tag{27}$$

When neglecting the difference between $\bar{V}_1^{L+}$ and $\bar{V}_1^{L}$, the first two terms of the right-hand side of eqn. 27 represent an expression applicable to the classical pseudo-binary system, and the last term represents the correction for the solubility of the carrier gas in the stationary phase.

Let us now consider the properties of the above correction term in greater detail. When omitting the trivial case of $x_2 \to 0$, the correction term acquires the value of unity for a number of the pairs of $\alpha - \beta$ and β, even at relatively high values of the molar fraction x_2 (approximately 0.2). In order to illustrate the case, calculated values of the corrections for several α, β and x_2 values are given in Table I.

TABLE I

VALUES OF THE CORRECTION FACTOR EXP $\{-[(\alpha - \beta)x_2 + \beta x_2^2]\}/(1 - x_2)$ FOR DIFFERENT VALUES OF α, β AND x_2

β	x_2	$\alpha - \beta$			
		0.5	*1.0*	*1.5*	*2.0*
0	0.05	1.027	1.001	0.977	0.952
	0.10	1.057	1.005	0.956	0.910
	0.15	1.091	1.013	0.939	0.871
	0.20	1.131	1.023	0.926	0.838
1	0.05	1.024	0.999	0.974	0.950
	0.10	1.046	0.995	0.947	0.901
	0.15	1.067	0.990	0.919	0.852
	0.20	1.087	0.983	0.890	0.805
2	0.05	1.021	0.996	0.972	0.948
	0.10	1.036	0.985	0.937	0.892
	0.15	1.043	0.968	0.898	0.833
	0.20	1.044	0.945	0.855	0.773

A situation characterized by a unit correction factor at $x_2 \neq 0$ corresponds to a case in which the effect of the increase in the amount of liquid phase in the column, brought about by the dissolved carrier gas, is just compensated for by that of the increase in the activity coefficient of the solute. This is the only way to explain, for example, the results of Sie *et al.*[3], who ascertained that the solubility of carbon dioxide in squalane did not affect the retention of benzene and methanol although the experimental data showed an appreciable solubility of carbon dioxide (as much as 20%, w/w).

Let us now compare the correction term defined by eqn. 27 with the formal correction introduced by Cruickshank and co-workers[19,20]. They employed the symmetrical convention for the activity coefficient of the solute. Hence, they worked with the activity coefficient γ_1^{+Pr}, and expanded the dependence of the logarithm of the activity coefficient of the solute on the amount of carrier gas dissolved in the stationary phase, *i.e.*, the function $\ln \gamma_1^{+Pr} = \ln \gamma_1^{+Pr}(x_2)$, into MacLaurin series:

$$\ln \gamma_1^{+Pr} = \ln \gamma_1^{Pr} + (\partial \ln \gamma_1^{+Pr}/\partial x_2)_0 \, x_2 + 0.5\,(\partial^2 \ln \gamma_1^{+Pr}/\partial x_2^2)_0 \, x_2^2 + \ldots \tag{28}$$

When comparing eqns. 28 and 19, it follows for the individual terms of Cruickshanks' correction that $\gamma_1^{Pr} = H_1^{Pr}/f_1^{0Pr}$, $(\partial \ln \gamma_1^{+Pr}/\partial x_2)_0 = \alpha - \beta$ and $(\partial^2 \ln \gamma_1^{+Pr}/\partial x_2^2)_0 = 2\beta$. In contrast to the formal expansion (eqn. 28), the application of eqns. 19 and 20 is of advantage in that they show the relationship between the value of $(\partial^2 \ln \gamma_1^{+Pr}/\partial x_2^2)_0$ as well as the deviations from an ideal infinitely dilute solution of the carrier gas in the binary carrier gas–stationary phase system. In accordance with eqn. 20, the above deviations are characterized by the value of β and can be determined from direct measurement of the solubility of the carrier gas in the stationary phase. In addition, eqns. 19 and 20 are automatically in compliance with the Gibbs–Duhem equation, which cannot be generally proved for the formal expansion 28.

The solubility of the carrier gas in the stationary phase is expressed by eqn. 14: after replacing γ_2^{*Pr} in the latter by eqn. 22, the molar fraction of carrier gas can be expressed explicitely. When assuming that $\bar{P} - Pr \approx \bar{P}$, there holds approximately the equation

$$x_2 \approx \frac{\varphi_2^0 \bar{P} \exp(-\overline{V}_2^{L} \bar{P}/RT)}{H_2^{Pr} - 2\beta \varphi_2^0 \bar{P} \exp(-\overline{V}_2^{L} \bar{P}/RT)} \tag{29}$$

The comparison with Cruickshank's power series $x_2 = \lambda P + \Phi P^2 + \varphi P^3 + \ldots$ is difficult and purposeless in this case. It holds very roughly that $\lambda \approx 1/H_2^{Pr}$ and $\Phi \approx 2\beta/(H_2^{Pr})^2$.

When neglecting the correction for the solubility in the case of a carrier gas of low solubility, eqn. 15 makes it possible to seek the pressure dependence of the fugacity coefficient of the solute in the solute–carrier gas mixture by employing the pressure dependence of V_g^{Tr}. In this case, eqn. 15 can be written as

$$\ln \varphi_1 = \ln\left(\frac{V_g^{Tr}}{z_2 (V_g^{Tr})_{\bar{P}=0}}\right) + \frac{\overline{V}_1^{L}}{RT} \cdot \bar{P} \tag{30}$$

In order to express this equation numerically, it is necessary to know the partial molar volume of the solute in the liquid phase. Even in this most favourable case, the mere knowledge of the pressure dependence of V_a^{Tr} is insufficient for the determination of the pressure dependence of the fugacity coefficient (the second cross-virial coefficient B_{12} in the simplest cases) of the solute–carrier gas mixture.

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