ENTROPY CHANGES DURING AN IDEAL GAS CHROMATOGRAPHIC SEPARATION

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INTRODUCTION

The theory of linear ideal partition chromatography envisages a concentration profile which does not vary while passing through the column. This axiomatic 'ideal' condition led to the qualitative conclusion that the chromatographic separation may be regarded as a reversible isentropic process which is not the reversal of diffusion [1]. However, later studies revealed that even though the ideal conditions of separation were imposed in the limit, the bandwidths of the separated bands emerging from an ideal column do not remain constant relative to the original widths [2]. Also, the assumption of idealization of the concentration profiles down the column becomes untenable for the simple reason that the column constitutes a conserved system demanding that the concentration must change on separation due to the expansion or contraction of the individual bands. It turns out, thus, that the isentropic nature of the chromatographic process derived simply on the basis of the partial entropies of the retained components only, without making any quantitative allowance for the contribution of the carrier gas and the stationary solvent [3], is an over-simplification of the real situation. Although much work has been done on molar thermodynamic functions of mixing for ideal and quasibinary systems [4, 5], the treatment in general is applicable to fields other than gas liquid chromatography.

The present investigation attempts to put forward a modified quantitative approach to study the isentropic/nonisentropic GLC separations, taking into account the entropy changes as a function of concentration profile variations arising from changes in the carrier gas flow in the retentive regions of an ideal column. In addition, the present work offers a mathematical analysis for estimating thermodynamic properties of multicomponent mixtures through GLC parameters. Excess thermodynamic properties [6] ($\Delta G^m, \Delta E^m$, etc.) may then be approached via this route.

THE ENTROPY OF THE MIXED BAND

This represents the difference of the combined entropy of the pure mobile and stationary phases confined in column length L over the combined entropy of the gas and liquid mixtures extending over the column length L which forms the chromatographic band. For ideal gas mixtures and simple solutions the total entropy change for both the phases, when the band is formed from its components at constant temperature and pressure, is given by

$$\Delta S^m = -k\left(N\sum x_j \ln x_j + N'\sum x'_j \ln x'_j \right), \qquad (1)$$

where k is the Boltzmann constant, $N = \Sigma N_j$, the total number of molecules in the gas phase, $N' = \Sigma N'_j$, the total number of molecules in the liquid phase and x_j

and x'_j the mole fractions of component j in the two phases.

For dilute solutions a linear relationship between the mole fraction x_j and x'_j for the retained components may be assumed, so that $N'_j/\Sigma N'_j = k_j N_j/\Sigma N_j$. Also the number of molecules in the liquid phase bears a constant ratio (α) to the number of molecules in the gas phase of the mixed band of fixed length L, such that $\alpha_j k_j = \lambda_j$, where k_j is the conventional capacity ratio. Hence the entropy of formation of the band composed of n retained components may be written as

RETAINED COMPONENTS

$$\Delta S^m = -kN\left(\sum_{j=1}^{n}\left\{(1+\lambda_j)x_j\ln x_j + \lambda_j x_j\ln k_j\right\}\right.$$

CARRIER GAS

$$+\left(1-\sum_{i=1}^{n}x_i\right)\ln\left(1-\sum_{i=1}^{n}x_i\right) \qquad (2)$$

STATIONARY PHASE

$$\left.+\alpha\left(1-\sum_{i=1}^{n}k_ix_i\right)\ln\left(1-\sum_{i=1}^{n}k_ix_i\right)\right],$$

where the subscript 'i' represents the continuous summation pertaining to mole fractions of the carrier gas and the stationary phase for any number, n, of components, irrespective of a retained component, j, which may acquire any single discrete value from 1 through n. From the standpoint of thermodynamics, the chromatographic separation of n retained components may, in general, be taken as a system of $n+2$ components, where the additional two components are the carrier gas (component 3) and the stationary phase (component 4). Thus, in the resolution of a binary band into components 1 and 2, the following conditions are operative: $N'_3 = N_4 = 0$ and $N = N_1 + N_2 + N_3$ and $N' = N'_1 + N'_2 + N'_4$. The entropy of formation of the binary mixed band may then be written as

$$\Delta S^m = -kN\left[\sum_{j=1}^{2}\left\{\ln\frac{x_j}{1-\sum_{i=1}^{2}x_i}\right.\right.$$

$$\left.+\lambda_j\ln\frac{k_jx_j}{1-\sum_{i=2}^{2}k_ix_i}\right\}x_j \qquad (3)$$

$$\left.+\ln\left(1-\sum_{i=1}^{2}x_i\right)+\alpha\ln\left(1-\sum_{i=1}^{2}k_ix_i\right)\right].$$

THE ENTROPY OF THE SEPARATED BANDS

Let us designate the state of separation by the superscript o, so that $x_j^o = N_j^o/N_j^o + N_3^o = N_j^o/N_{j,3}^o$ and $\alpha_j^o = N_j'^o + N_4'^o/N_j^o + N_3^o = N_{j,4}'/N_{j,3}^o$ (total number of molecules in the liquid phase/total number of molecules in the gas phase for the jth band for component j). Assuming, as before, a linear proportionality between x_j^o and $x_j'^o$ and letting $\lambda_j^o = \alpha_j^o k_j$, the difference in entropy (ΔS_j^o) between the combined entropy of the gas and liquid mixtures containing the retained component j may be expressed as

$$\Delta S_j^o = -k\left[N_{j,3}^o\left\{x_j^o\ln\frac{x_j^o}{1-x_j^o}\right.\right.$$

$$+\ln(1-x_j^o)+\lambda_j^o x_j^o\ln\frac{k_jx_j^o}{1-k_jx_j^o} \qquad (4)$$

$$\left.\left.+\alpha_j^o\ln(1-k_jx_j^o)\right\}\right].$$

Putting $N_{j,3}^o = NL_j^o/L$, as demanded by the conservation of matter, the total entropy difference, $\Delta S = \Sigma \Delta S_j^o$, for the individual bands may be expressed as

$$\Delta S^o = -kN\left[\sum_{j=1}^{2}\frac{L_j^o}{L}\left\{x_j^o\ln\frac{x_j^o}{1-x_j^o}\right.\right.$$

$$+\ln(1-x_j^o)+\lambda_j^o x_j^o\ln\frac{k_jx_j^o}{1-k_jx_j^o} \qquad (5)$$

$$\left.\left.+\alpha_j^o\ln(1-k_jx_j^o)\right\}\right].$$

The band lengths in the mixed and the separated state are related to each other [2] by

$$\frac{L_j^o}{L} = \frac{x_j}{x_j^o} = \left[1+\frac{k'_{j\pm1}x_{j\pm1}^o}{k'_j-k'_{j\pm1}}\right] = f_j, \qquad (6)$$

where the plus sign refers to $j=1$ and the negative sign to $j=2$. Making this substitution in Equation (5), we obtain

$$\Delta S^o = -kN\sum_{j=1}^{2}\left[\left\{\ln\frac{x_j^o}{1-x_j^o}+\lambda_j^o\ln\frac{k_jx_j^o}{1-k_jx_j^o}\right\}\right.$$

$$\left.f_jx_j^o+f_j\ln(1-x_j^o)+\alpha_j^o f_j\ln(1-k_jx_j^o)\right]. \qquad (7)$$

Hence, for a binary mixture the entropy of separation, ΔS, associated with kinematically expanded and contracted bands can be obtained by subtracting Equation (3) from Equation (7)

$$\Delta S = -kN \sum_{j=1}^{2} \left\{ f_j x_j^0 \ln \frac{1 - \sum_{i=1}^{2} f_i x_i^0}{f_j(1 - x_j^0)} \right.$$

$$+ f_j \ln(1 - x_j^0) - \ln\left(1 - \sum_{i=1}^{2} f_i x_i^0\right)\right\}$$

$$+ \left\{ \lambda_j^0 \ln \frac{k_j x_j^0}{1 - k_j x_j^0} \right. \tag{8}$$

$$\left. - \lambda_j \ln \frac{k_j f_j x_j^0}{1 - \sum_{i=1}^{2} k_i f_i x_i^0} \right\} f_j x_j^0$$

$$+ \left\{ \alpha_j^0 f_j \ln(1 - k_j x_j^0) - \alpha \ln\left(1 - \sum_{i=1}^{2} k_i f_i x_i^0\right)\right\}.$$

DISCUSSION

According to the theory of partition chromatography, the assumptions for ideal separation are: (i) instantaneous equilibrium (zero driving force); (ii) absence of irreversible effects; (iii) piston-like flow profile; (iv) uniformity of column packing. These coupled with the requirement of plug injection have so far been regarded not only necessary but also sufficient conditions to ensure resolution of a given mixture into sharp bands having the same width as that of the initial 'mixed-band'. However, it has been theoretically shown [2] that even these 'ideal' conditions do not warrant invariant concentration profiles — a fact applicable even to a simple binary system. As the two components in a binary system become more and more similar with regard to their solubilities, the separation is rendered more and more difficult, approaching, in the limit, a state of no separation as the two solubilities become identical. The chromatographic column not only fails to separate species with exactly zero retentions, but it is also inherently incapable of distinguishing between them. Thus, from the chromatographic angle, components with zero solubilities may be conceived as a single species even though these may be chemically different.

In view of this, let us now consider the case of a binary mixture in which only one of the components is retained in the stationary phase, say with $k_1 > 0$ and $k_2 = 0$. As component 2 and the carrier gas have zero retentions in the stationary solvent, they may be regarded as a single 'composite' species. It follows that the retained component in such a binary mixture should travel down the column as a band of constant length and invariant concentration. Realizing that after separation the unretained component is simply replaced by another unretained component (called the carrier gas), the entropy changes associated with the retained component in the mixed and the separated states for the two phases should be the same. Consequently, the net entropy change, during chromatographic separation of a binary system with $k_2 = 0$, should be zero. On putting $k_2 = 0$ (under which condition $\lambda_j^0 = \lambda_j$ and $\alpha = \alpha_j^0$) the r.h.s. expression given in Equation (8) vanishes, showing thereby that it is only the binary chromatographic process with one retained component which behaves isentropically, as has been shown previously [3]. Thus, only binary chromatographic separations can be labelled as 'isentropic' under constraining conditions of the type cited above, but for all other real systems one should invariably expect finite entropy changes (given in magnitude by Equation (8)) associated with the separation process.

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