APPLICATION OF CONVENTIONAL THERMODYNAMIC APPROXIMATIONS TO MIXED-SOLVENT GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

Conventional thermodynamic approximations indicate a general non-linear dependence of partition coefficient on stationary-phase composition in mixed-solvent gas–liquid chromatography (GLC). The deviations from linearity have been calculated for varying circumstances, and the fact that many reported experimental measurements appear to conform to an approximately linear relation is explained by an extrapolation of solubility-parameter theory. The same thermodynamic treatment has been used to predict the behaviour of partially miscible stationary phases in GLC.

INTRODUCTION

About twenty years have elapsed since Ashworth and Everett[1] showed that established thermodynamic theory, namely the Flory–Huggins theory, could be usefully applied to the binary solutions encountered in simple gas–liquid chromatographic (GLC) systems. It is therefore surprising that extension of their treatment to mixed-solvent (or mixed stationary-phase) GLC should only have been reported relatively recently[2,3], and that the partitioning characteristics of such columns in GLC should so long have been the subject of uncertainty[4]. For example, some ten years ago there was controversy as to whether a column packing prepared by coating the support with a mixture of two stationary phases would show the same partition coefficient for a given solute as a packing prepared by mechanically mixing the two separately coated supports (these two types of columns have been described as mixed-solvent and mixed-bed columns). The theory of Keller and Stewart[5], who suggested no difference in behaviour, was criticised by Young[6] who came to the opposite conclusion. Surprisingly, experimental results seem to have been inconclusive[4] in this matter.

A bold hypothesis, based on examination of reported results of a large number of mixed-solvent GLC systems, was put forward by Purnell and co-workers[7,8]. They suggested that existing thermodynamic theory could not account for the behaviour of mixed-solvents in GLC work, since they claimed that the dependence of the parti-

tion coefficient, $K_{R(2,3)}$, on stationary phase composition was much simpler than any derivable from conventional theory. A simple linear relationship was suggested,

$$K_{R(2,3)} = \varphi_2 K_{R(2)} + (1 - \varphi_2) K_{R(3)} \tag{1}$$

$K_{R(2)}$, $K_{R(3)}$ are the values of K_R in the pure solvents 2 and 3, whilst φ_2 is the volume fraction of solvent 2 in the mixed stationary phase.

A linear relation such as eqn. 1 would indeed imply that mixed-solvent and mixed-bed columns should be indistinguishable in their partitioning characteristics. Whilst, admittedly, this relation cannot be derived from conventional theory, Martire[9] briefly discussed theoretical circumstances which might approximate to such a linear relation. More recently Laub et al.[10] have applied Flory's more sophisticated solution theory to GLC systems involving n-alkane solutes in a binary mixture of large molecule n-alkane solvents and have shown that eqn. 1 is obeyed within 1% deviation.

If eqn. 1 is to be regarded as an empirical approximation, the "mixed-solvent linear approximation", it is important quantitatively to examine the degree of approximation involved and the circumstances under which it might be a very poor approximation. Published examples of the latter range from some results of Littlewood and Wilmott[11] in 1966 to those of Perry and Tiley[12] in 1978. In both cases, systems showing deviations from linearity of 20–30% were reported and the use of eqn. 1 could lead to very erroneous conclusions.

THEORY AND CALCULATIONS

Predictions based on conventional thermodynamics of ternary solutions

The starting point is the usual inverse relation between the GLC partition coefficient and the activity coefficient at infinite dilution of the solute, γ_1^∞,

$$K_R = a/(\gamma_1^\infty V_s) \tag{2}$$

where V_s is the molal volume of the stationary phase and a is constant for a given solute at fixed temperature. Since GLC systems invariably comprise components of very different molal volumes, a useful first approximation for activity coefficients in non-ideal multicomponent solutions is given[13] by,

$$\ln \gamma_i = V_i \Sigma_j \Sigma_k (\chi_{ij} - \tfrac{1}{2}\chi_{jk}) \varphi_j \varphi_k + [\ln (\varphi_i/x_i) + 1 - \varphi_i/x_i] \tag{3}$$

The symbols χ and φ represent mole and volume fractions respectively. The second term in eqn. 3 is the Flory–Huggins combinatorial term, whilst the first term originates from the Hildebrand–Scatchard treatment where the χ_{ij} parameters quantify the energetic interaction between components i and j and V_i is the molal volume. Superficially one may say that the more positive the value of χ_{ij}, the less the "affinity" between the components i and j.

Nobody today would claim that eqn. 3 is anything other than a first approximation to a comprehensive thermodynamic treatment of solutions. When non-spherical and/or polar molecules are involved, it is unlikely that the χ terms can be

regarded as unique composition-independent parameters, related solely to energetic interactions.

That, despite its apparent complexity, eqn. 3 leads to a relatively straight-forward expression for partition coefficients in mixed solvents, was demonstrated by Perry and Tiley[12] who derived the relation,

$$\ln K_{R(2,3)} = \varphi_2 \ln K_{R(2)} + (1 - \varphi_2) \ln K_{R(3)} + \varphi_2 (1 - \varphi_2) \chi, \tag{4}$$

where $\chi = V_1 \chi_{23}$, and χ_{23}, the solvent-solvent interaction parameter, should be in-dependent of composition and of the nature of the solute. In fact these workers showed that using aliphatic and aromatic hydrocarbon solutes on mixed dinonyl phthalate–2,4,6-trinitrotoluene columns, eqn. 4 could be usefully applied despite the strongly polar nitro groups on one solvent.

It is not possible mathematically to approximate eqn. 4 to the linear form of eqn. 1 except for the very special case of $K_{R(2)} \approx K_{R(3)}$ and $\chi_{23} \simeq 0$. Otherwise, de-pending on the value of $K_{R(2)}/K_{R(3)}$, the "K_R ratio", and of χ, the $K_R - \varphi$ plot may be concave to the φ axis (positive curvature), convex (negative curvature) or may show a point of inflection.

Since mathematical analysis revealed no simple relation between eqns. 4 and 1, resort was made to simple calculation. The percentage mean deviation from linear behaviour, as predicted by eqn. 4 and defined in Appendix I, was computed for varying values of the K_R ratio and of χ. The results are shown in Fig. 1. The maximum deviations from linearity, which are not necessarily around the mid-composition point are a factor of 1.3–2.3 greater than the mean deviations shown.
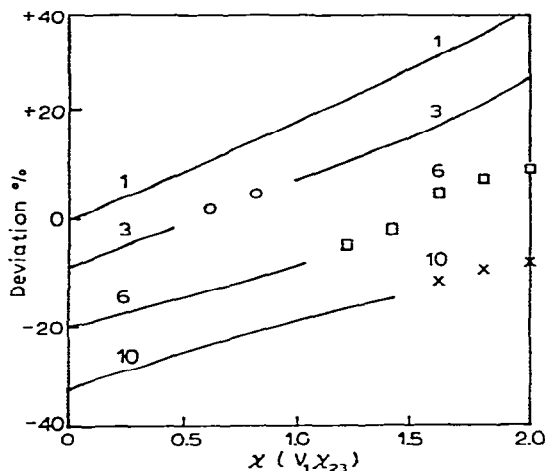

Fig. 1. Mean deviation from eqn. 1 as predicted by eqn. 4, with solvent–solvent interaction as in-dependent variable and K_R ratio as parameter. Points $\bigcirc$, $\square$ and $\times$ result from inflected K_R-φ plots.

Since eqn. 4 gives K_R as a continuous non-linear function of composition, it can never (except in the special case mentioned above) predict a mathematically zero mean deviation from linearity. The change from negative to positive curvature, which is shown in Fig. 1 with increasing χ value, is necessarily accompanied by circumstances in which the $K_R - \varphi$ plots show a point of inflection, where the mean

deviation may be small but never zero. Hence the curves in Fig. 1 are discontinuous in the region of zero mean deviation.

An example of an inflected $K_R - \varphi$ plot is shown in Fig. 2 where the computed mean deviation is not particularly small (9%) and the maximum deviation is 20%. It is possible for a system of this kind that experimental measurements using only three or four composition points might lead to the conclusion that a linear relation is obeyed. Moreover, since the point of inflection occurs at $\varphi = 0.55$ with approximately zero deviation from the linear approximation, it means that a single measurement around the mid-composition point would almost certainly lead to a similar erroneous conclusion.
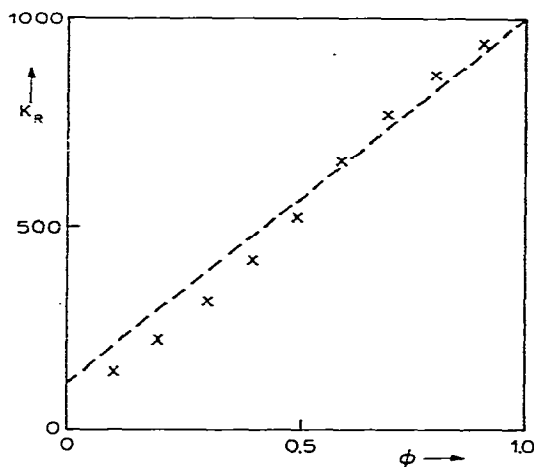

Fig. 2. Example of an inflected K_R-φ plot. Points $\times$ calculated from eqn. 4 with $\chi = 2.0$. Dotted line based on eqn. 1.

Even allowing for understandable misjudgments of this kind and for experimental error, examination of Fig. 1 suggests that significant deviations from a linear relation should be the rule rather than the exception, and therefore significant differences in behaviour of mixed-solvent and mixed-bed GLC columns should have been observed. Yet this conclusion is generally contrary to published work on mixed-solvent columns where many cases of approximately linear behaviour are known[8], nor is it consistent with experimental results on the two types of column. This anomaly can be resolved without resorting to any new and special theory for GLC systems.

The mixed-solvent interaction parameter and the K_R ratio

In Fig. 1, the χ (= $V_1\chi_{23}$) value ranges from 0–2.0. Zero is the "ideal" value, and the maximum of 2.0 was chosen because of partial miscibility considerations which are discussed later. The range of the K_R ratio is 1–10 which covers most but not all GLC systems. However, the assumption that the behaviour of GLC mixed-solvent systems is adequately represented by Fig. 1 implies that χ_{23} and the K_R ratio are two completely uncorrelated and independent variables. Such an hypothesis is unlikely to be true.

If we consider the case where the combinatorial terms are the same in the