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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 Everett¹ 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 uncertainty⁴. 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 Stewart⁵, who suggested no difference in behaviour, was criticised by Young⁶ who came to the opposite conclusion. Surprisingly, experimental results seem to have been inconclusive⁴ 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,

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

$K_{R(2)}$, $K_{R(3)}$ 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, Martire⁹ 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 Wilmott¹¹ in 1966 to those of Perry and Tiley¹² 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^∞ ,

$$K_R = a/(\gamma_1^\infty V_s) \quad (2)$$

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 given¹³ by,

$$\ln \gamma_i = V_i \sum_j \sum_k (\chi_{ij} - \frac{1}{2} \chi_{jk}) \varphi_j \varphi_k + [\ln (\varphi_i/x_i) + 1 - \varphi_i/x_i] \quad (3)$$

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 straightforward expression for partition coefficients in mixed solvents, was demonstrated by Perry and Tiley¹² who derived the relation,

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

where $\chi = V_1 \chi_{23}$, and χ_{23} , the solvent-solvent interaction parameter, should be independent 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 $\chi_{23} \approx 0$. Otherwise, depending 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.

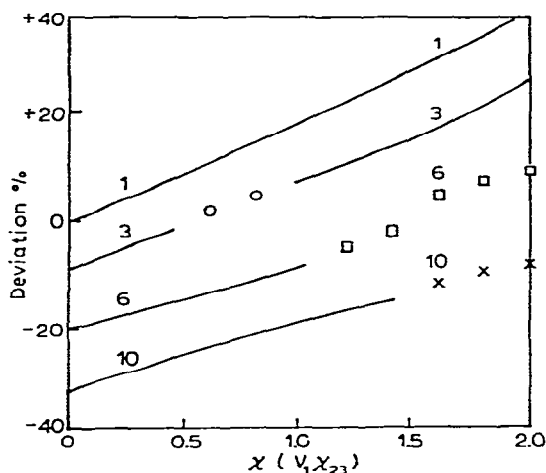


Fig. 1. Mean deviation from eqn. 1 as predicted by eqn. 4, with solvent-solvent interaction as independent variable and K_R ratio as parameter. Points \circ , \square and \times result from inflected $K_R - \varphi$ plots.

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 $K_R - \phi$ 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 $\phi = 0.55$ 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.

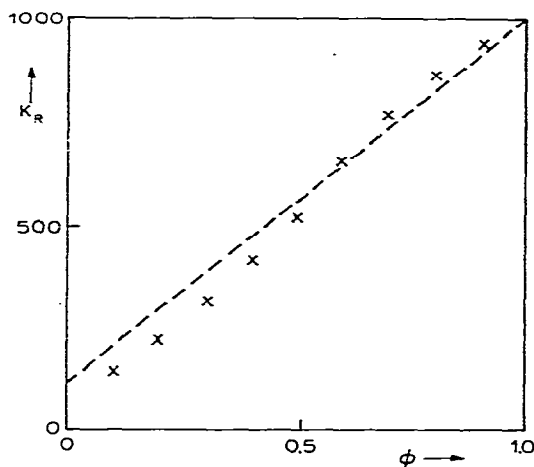


Fig. 2. Example of an inflected $K_R - \phi$ plot. Points \times calculated from eqn. 4 with $\chi = 2.0$. Dotted line based on eqn. 1.

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 known⁸, 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 $\chi (= V_1\chi_{23})$ 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

two solvents ($V_2 \approx V_3$), then the K_R ratio is dependent on the individual solute-solvent interactions, χ_{12} and χ_{13} . If the K_R ratio is close to unity then χ_{12} and χ_{13} are approximately the same, and under these circumstances a low value of χ_{23} is much more probable than a high value. Indeed under these circumstances one might expect χ_{23} to be close to zero, which would then result in an approximately linear K_R - φ plot.

A quantitative correlation of the K_R ratio with χ_{23} can be derived from solubility parameter theory in its simplest form which postulates that,

$$\chi_{ij} = (\delta_i - \delta_j)^2/RT \quad (5)$$

in which δ_i and δ_j , the solubility parameters, are unique characteristics of components i and j . From eqn. 5, provided δ_1 , the solubility parameter of the solute, is less than both δ_2 and δ_3 for the solvents, it follows that,

$$\chi_{23} = (\chi_{12}^\dagger - \chi_{13}^\dagger)^2 \quad (6)$$

The provision will normally, but not necessarily, apply to GLC systems¹². Combining eqns. 3 and 6 as shown in Appendix II, a relationship between χ_{23} and the K_R ratio can be demonstrated involving χ_{12} as an independent parameter.

Selecting a suitable range of values of χ_{12} , further calculations were performed of the predicted deviations from the mixed-solvent linear approximation and the results are shown in Fig. 3. The maximum value of $\chi_{12} = 15 \text{ mol dm}^{-3}$ is justified on the basis of Appendix II which shows that normally for $K_{R(2)} > K_{R(3)}$ then $\chi_{13} > \chi_{12}$, and since a value of 15 mol dm^{-3} implies considerable "negative affinity" between solute and solvent 2, then even greater "negative affinity" would exist for solvent 3. In fact for most GLC mixed-solvent systems one might expect χ_{12} to be in the range 0 – 6 mol dm^{-3} giving χ_{13} in the range 0 – 30 mol dm^{-3} for K_R ratio 1 – 10 .

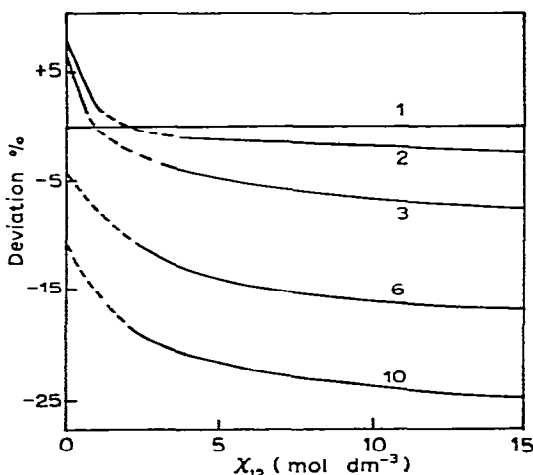


Fig. 3. Mean deviation from eqn. 1 as predicted by eqn. 4, with solute-solvent interaction as independent variable and K_R ratio as parameter. Dotted lines represent approximately the regions of inflected K_R - φ plots.

Examination of Fig. 3 shows that provided the K_R ratio < 3 , the mean deviation from linearity is not much in excess of 5% for a considerable range of χ_{12} and this should cover many reported studies (there is an exception to this mentioned below). As the K_R ratio increases, the linear approximation becomes less satisfactory, although at low χ_{12} values, the inflected K_R - φ plots, discussed previously, would be encountered.

Appendix II shows that, on this treatment, χ_{12} and the K_R ratio are not the only two parameters which determine the shape of the K_R - φ plot. The molal volumes of the solvents V_2 and V_3 together with that of the solute, V_1 , inevitably have some effect. Further extensive computations were carried out varying these parameters, but the main conclusions of the immediately preceding paragraph still held except in one respect. When $V_3 < V_1$, then large ($> 20\%$) positive curvature in the K_R - φ plot is predicted at low χ_{12} values for systems where the K_R ratio is close to unity. This phenomenon has been reported¹² for the GLC systems xylene-dinonyl phthalate-2,4,6-trinitrotoluene where the molal volumes of the xylenes exceed that of 2,4,6-trinitrotoluene.

Partition coefficients in partially miscible solvent systems

Eqn. 4 can only apply to a homogeneous mixture of the two solvents, and when χ_{23} becomes sufficiently large, solution theory predicts phase separation. If this occurs then the partition coefficient of the solute in the two-phase solvent medium will be linearly related to the partition coefficients in the two phases (conjugate solutions) thus:

$$K_{R(2,3)} = \varphi^I K_R^I + \varphi^{II} K_R^{II} \quad (7)$$

where the superscripts refer to the two liquid phases I and II.

Assuming zero excess volume of each phase, the volume fractions of the phases, φ^I and φ^{II} , will be related to the system composition variable φ_2 , by the usual material balance equations:

$$\varphi^I = (\varphi_2^{II} - \varphi_2)/(\varphi_2^{II} - \varphi_2^I); \varphi^{II} = 1 - \varphi^I \quad (8)$$

Combining eqns. 7 and 8 gives the relation,

$$K_{R(2,3)} = [(\varphi_2^{II} - \varphi_2)K_R^I + (\varphi_2 - \varphi_2^I)K_R^{II}]/(\varphi_2^{II} - \varphi_2^I) \quad (9)$$

Since the phase composition parameters, φ_2^I and φ_2^{II} , are fixed for a given partially miscible system at fixed temperature and pressure, as also are K_R^I and K_R^{II} (see below), it follows that eqn. 9 reduces to a linear K_R - φ relation for the two-phase region, thus,

$$K_{R(2,3)} = C_0 + C_1\varphi_2 \quad (10)$$

The coefficients C_0 and C_1 are obviously not the same as in eqn. 1, and are given by:

$$C_0 = (\varphi_2^{II}K_R^I - \varphi_2^IK_R^{II})/(\varphi_2^{II} - \varphi_2^I)$$

$$C_1 = (K_R^{II} - K_R^I)/(\varphi_2^{II} - \varphi_2^I)$$

The partition coefficients in the two liquid phases, K_R^I and K_R^{II} will be given by eqn. 4 where the composition parameters used in this equation must now be φ_2^I and φ_2^{II} , the compositions of the two conjugate solutions. Accepting eqn. 3 for activity coefficients, the phase compositions are determined by the usual thermodynamic condition for equilibrium, and are dependent on V_2/V_3 and χ_{23} , the solvent-solvent size ratio and interaction parameter, as shown in Appendix III.

Using selected values of the independent variables, examples of the behaviour predicted for a partially miscible solvent system are shown in Fig. 4. Again it can be seen that for such a system, the K_R - φ plots can show positive, negative or approximately zero departure from linearity depending on the K_R ratio. The difference between the behaviour predicted for a completely miscible system and that for partial miscibility is the existence of a linear portion in the two-phase composition region, as predicted by eqn. 10. Phase separation will therefore lead to a smaller mean deviation from linearity than otherwise would occur. It would, of course, also be possible with solvents of very limited mutual solubility (e.g. $\varphi_2^I < 0.01$ and $\varphi_2^{II} > 0.99$) for the K_R - φ plot to be close to linearity over the whole system composition range irrespective of the K_R ratio, but this behaviour would indeed be restricted to such solvents of almost total immiscibility.

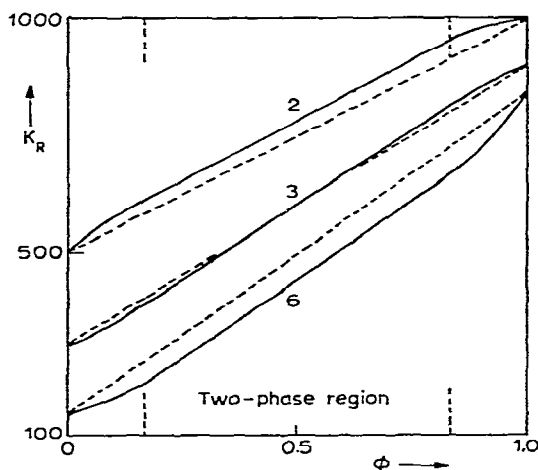


Fig. 4. Examples of predicted K_R - φ plots for a partially miscible symmetric system, with K_R ratio as parameter. Full lines calculated from eqns. 4 and 10 as described in the text with $V_2 = V_3 = 0.4$ $\text{dm}^3 \text{mol}^{-1}$, $V_1 = 0.1 \text{dm}^3 \text{mol}^{-1}$, and $\chi_{23} = 6$ (see Table I). Dotted lines based on eqn. 1.

DISCUSSION

The application of the conventional thermodynamic approximation of eqn. 3 shows that the GLC partition coefficient can never be a strictly linear function of stationary phase composition for mixed solvents, except in the extreme case of complete solvent immiscibility. However, for systems where K_R values in the two pure solvents are not widely different, e.g. within a factor of 3, then calculation shows that there might be a wide range of systems where linear behaviour should be observed within approximately 5%. As the K_R ratio increases, greater deviations from

linear behaviour would normally be expected, except that under some circumstances, inflected K_R - φ plots are predicted which might be mistaken for a linear relation. It follows that the mixed-solvent linear approximation of eqn. 1 must be used with considerable caution in predicting the behaviour of a mixed-solvent GLC column. The fact that several solutes may conform to the approximation for a given solvent system does not imply that all solutes will necessarily do so for the same system. Additionally, the circumstances which lead to considerable deviations from the linear composition relation will also yield significant differences in behaviour between mixed-solvent columns and mixed-bed columns.

That eqn. 3 is only a first approximation to a comprehensive thermodynamic treatment must be reiterated. Based as it is on the Hildebrand-Scatchard regular solution model, eqn. 3 takes no account of specific "chemical" interactions either between solute and solvent or solvent and solvent. The formation of molecular complexes, whether by hydrogen-bonding or by charge transfer are excluded from the treatment. Weak complexing may not significantly affect¹² the application of eqn. 4, but would certainly tend to invalidate any conclusions based on solubility-parameter theory such as given in Appendix II. Even in the absence of specific interactions or of polar forces, eqn. 3 is by no means a wholly adequate representation of the molecular thermodynamics of liquid solutions¹⁰. Nevertheless, it is the contention of this paper that the use of eqn. 3 and its corollary, eqn. 4, will give a better insight into the behaviour of mixed-solvent GLC columns than any purely empirical approximation.

Finally, it will be appreciated that the thermodynamic treatment which has been used is that applicable to bulk liquid phases. No account has been taken of interfacial adsorption effects. For a homogeneous solvent system used at fairly high liquid loading on an inactivated support, there is no reason to believe that significant effects should occur¹². But if liquid phase separation occurs, adsorption at the liquid-liquid interface might be significant if a relatively large interfacial area is created. The mechanism of phase separation is likely to involve nucleation of the second liquid phase at either the solid-liquid or gas-liquid interface or both, but the physical "structure" of the resulting "thin film" two-phase system remains a subject for speculation.

APPENDIX I

Quantification of the deviation from the mixed-solvent linear approximation

$$\text{Deviation } (\Delta K_R) = [K_R(\text{eqn. 4}) - K_R(\text{eqn. 1})]/K_R(\text{eqn. 1})$$

$$\text{Mean deviation } (\%) = \Sigma |100\Delta K_R|/10$$

where ΔK_R is computed at 0.1 intervals of φ from 0 to 1. Whilst the mean deviation was calculated as an absolute value, an algebraic sign was then ascribed to it depending on whether the ΔK_R values were wholly positive (concave K_R - φ plot) or wholly negative (convex K_R - φ plot). For cases where ΔK_R changed sign (inflected K_R - φ plot), an algebraic sign was assigned to the mean deviation corresponding to that for the majority of the ΔK_R values.

Substituting the expressions for K_R from eqns. 4 and 1, with $\varphi_2 = \varphi$,

$$\Delta K_R = \frac{\exp[\varphi \ln K_{R(2)} + (1 - \varphi) \ln K_{R(3)} + \varphi(1 - \varphi)\chi]}{\varphi K_{R(2)} + (1 - \varphi)K_{R(3)}} - 1$$

Putting $K_{R(2)}/K_{R(3)} = f$, the " K_R ratio",

$$\begin{aligned} \Delta K_R &= \frac{\exp[\varphi \ln f - \ln f + \ln K_{R(2)} + \varphi(1 - \varphi)\chi]}{\varphi K_{R(2)} + (1 - \varphi)K_{R(2)}/f} - 1 \\ &= \frac{K_{R(2)} \exp[(\varphi - 1) \ln f + \varphi(1 - \varphi)\chi]}{K_{R(2)}[\varphi + (1 - \varphi)/f]} - 1 \\ &= \frac{f \exp[(1 - \varphi)(\varphi\chi - \ln f)]}{\varphi(f - 1) + 1} - 1 \end{aligned}$$

Hence the deviation from linearity is dependent on the K_R ratio and on χ , and is independent of the absolute value of $K_{R(2)}$ or of $K_{R(3)}$. It is noteworthy that using $f = 1.35$ and $\chi = 0$, which are effectively the parameters used in the studies of Laub *et al.*¹⁰, yields a deviation of -1.1% at $\varphi = 0.5$, which is in good agreement with their sophisticated calculations.

APPENDIX II

Relationship between χ_{23} and the K_R ratio

As shown elsewhere¹², the Flory-Huggins term in eqn. 4 may be written as,

$$\text{FH}(r_i) = -\ln r_i + 1 - 1/r_i \quad (11)$$

where $r_i = V_s/V_i$ and $V_s = \sum x_i V_i$

At infinite dilution of the solute, component 1, in either of the pure solvents, eqn. 3 gives¹²,

$$\ln \gamma_{1(2)}^\infty = \text{FH}[r_{1(2)}] + V_1 \chi_{12}$$

$$\ln \gamma_{1(3)}^\infty = \text{FH}[r_{1(3)}] + V_1 \chi_{13}$$

Substituting in eqn. 2,

$$\ln K_{R(2)} = \ln a - \text{FH}[r_{1(2)}] - V_1 \chi_{12} - \ln V_2$$

$$\ln K_{R(3)} = \ln a - \text{FH}[r_{1(3)}] - V_1 \chi_{13} - \ln V_3$$

Subtracting these two expressions and putting $K_{R(2)}/K_{R(3)} = f$,

$$\ln f = \text{FH}[r_{1(3)}] - \text{FH}[r_{1(2)}] + \ln(V_3/V_2) - V_1 \chi_{12} + V_1 \chi_{13}$$

Substituting for the Flory-Huggins functions from eqn. 11,

$$\chi_{13} = \frac{\ln f}{V_1} + \frac{V_2 - V_3}{V_2 V_3} + \chi_{12} \quad (12)$$

Taking eqn. 12 along with the solubility parameter relation eqn. 6, gives two equations relating the four parameters χ_{12} , χ_{13} , χ_{23} and f . Therefore if we take χ_{12} , the solute-solvent interaction parameter as an independent variable along with the K_R ratio, f , then the value of χ_{23} , the solvent-solvent interaction parameter will be determined via eqns. 12 and 6. This has been done for the computations which are shown graphically in Fig. 3.

It will be appreciated that choosing the K_R ratio as an independent parameter is done for the convenience of comparing theory and experiment, since it is an immediately observable quantity. The reality of the situation is that the two solute-solvent interaction parameters, χ_{12} and χ_{13} , together with the respective molal volumes, physically determine the observed K_R ratio, and based on this hypothesis also determine the mixed-solvent behaviour.

APPENDIX III

Liquid phase compositions in a partially miscible system

For the solvent 2-solvent 3 system when phase separation occurs, the usual thermodynamic condition for equality of component-activities in each phase must apply, which can be written as,

$$\gamma_2^I x_2^I = \gamma_2^{II} x_2^{II} \quad \text{and} \quad \gamma_3^I (1 - x_2^I) = \gamma_3^{II} (1 - x_2^{II}) \quad (13)$$

Assuming that eqn. 3 applies,

$$\begin{aligned} \ln \gamma_2^I &= FH(r_2^I) + (1 - q_2^I)^2 V_2 \chi_{23} \\ \ln \gamma_3^I &= FH(r_3^I) + (q_2^I)^2 V_3 \chi_{23} \end{aligned} \quad (14)$$

and similarly for phase II.

The FH functions will be given by eqn. 11, *e.g.*

$$FH(r_2^I) = -\ln r_2^I + 1 - 1/r_2^I,$$

where $r_2^I = V^I/V_2$ and $V^I = x_2^I V_2 + (1 - x_2^I) V_3$.

Since zero excess volume is implicit in this treatment, mole fraction and volume fractions are simply related, and combination of relations 14 and 13 results in a pair of non-linear simultaneous equations for the two unknowns, which may be either x_2^I and x_2^{II} or q_2^I and q_2^{II} .

The independent parameters are V_2 , V_3 and χ_{23} .

Numerical solution of this problem is computationally possible (a straightforward grid search proved as satisfactory as any method), but the problem reduces

to just one non-linear equation for the symmetric case of $V_2 = V_3$, since then $x_2^I = \varphi_2^I$ etc. and $\varphi_2^{II} = 1 - \varphi_2^I$. Some results for this case are shown in Table I.

TABLE I

COMPOSITION OF PARTIALLY MISCIBLE PHASES FOR A SYMMETRIC SYSTEM WHERE $V_2 = V_3 = 0.4 \text{ dm}^3 \text{ mol}^{-1}$ AND $V_1 = 0.1 \text{ dm}^3 \text{ mol}^{-1}$

$\chi_{23} (\text{mol dm}^{-3})$	$V_2\chi_{23}$	φ_2^I	$\chi (= V_1\chi_{23})$
12.5	5	0.0072	1.25
10	4	0.0213	1.0
7.5	3	0.0707	0.75
6	2.4	0.1707	0.6
5.5	2.2	0.2485	0.55
5	2.0	No phase separation	0.5

It is apparent that, for the symmetric case, phase separation occurs at $\chi_{23} \approx 5 \text{ mol dm}^{-3}$, and, with $V_1 = 0.1 \text{ dm}^3 \text{ mol}^{-1}$, the maximum value of χ in eqn. 4 for a miscible system would therefore be about 0.5. However for asymmetric systems ($V_2 \neq V_3$), larger χ_{23} values are possible without phase separation. For example, dinonyl phthalate ($V_2 = 0.45 \text{ dm}^3 \text{ mol}^{-1}$), and 2,4,6-trinitrotoluene ($V_3 = 0.15 \text{ dm}^3 \text{ mol}^{-1}$) are completely miscible¹² at 82° with $\chi_{23} \approx 8 \text{ mol dm}^{-3}$, and with the xylenes as solutes ($V_1 \approx 0.2 \text{ dm}^3 \text{ mol}^{-1}$) then χ values of around 1.6 are produced.

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