Theoretical evaluation of k_p and λ in g.p.c.: A criterion to define ideal reference systems

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From a thermodynamic point of view, theoretical expressions for the distribution coefficient of solute–gel interactions in g.p.c., k_p, and the preferential sorption coefficient, λ, have been developed. In the light of these expressions, a criterion to define an ideal reference system in which solutes are separated solely by steric exclusion, $k_p=1$, has been reached. This criterion implies that $g_{12}^{\circ}+g_{13}^{\circ}=1$ and $\lambda=0$ (g_{ij}° being the Flory–Huggins interaction parameters). From literature data of k_p, λ values have been calculated. These values vary with molecular weight as in the case of solvent(1)/solvent(2)/polymer(3) systems.

(**Keywords:** distribution coefficient; solute–gel interactions; sorption coefficient; gel permeation chromatography)

INTRODUCTION

In g.p.c. on organic packings, the universal calibration concept[1] is well established for different polymers and solvents provided that the solvents are good for the polymers. However, when the polymers are eluted in poor or 'theta' solvents, solute–gel interactions become important and secondary mechanisms appear (adsorption and partition[2–4]) with the retention volume, V_R, being displaced to high V_R values with respect to universal calibration. In other cases, because of incompatibility between solute polymer and gel, V_R values are shifted toward smaller retention volumes[5].

The adsorption of the solute polymer onto the gel or the opposite case of incompatibility between solute polymer and gel can be related to preferential or selective sorption. In this way, a theoretical expression for the distribution coefficient of solute–gel interactions, k_p, has been recently derived[5].

In this paper we present a more extended theoretical procedure to evaluate k_p, the expressions reached are equivalent to those obtained previously. Furthermore, the thermodynamic treatment has been also applied in order to derive an equation for the preferential sorption coefficient, λ.

The aim of this work is to arrive at a criterion defining a reference system in which solutes are separated solely by steric exclusion, $k_p=1$. This criterion implies that for a solvent(1)/solute polymer(2)/gel(3) system $g_{13}^{\circ}+g_{12}^{\circ}=1$ (g_{ij}° being the Flory–Huggins interaction parameters at infinite dilution) and $\lambda=0$.

On the other hand, from literature k_p values[2–4,6] we obtain λ values. When $k_p>1$ (compatibility between the solute polymer and gel) the λ values are negative. These values vary with molecular weight as in the case of solvent(1)/solvent(2)/polymer(3) systems.

THERMODYNAMIC CALCULATIONS

A polymer chain fractionation by g.p.c. on swelling sorbents can be regarded as a polymeric ternary system, constituted by solvent (1)/polymeric solute (2)/gel matrix (3) (swollen gel). Under usual chromatographic conditions and from a thermodynamic point of view this system can be considered as being formed by two phases coexisting in equilibrium:

(1) A 'binary phase', constituted by the polymer solution outside the pore (mobile phase) or inside the pore but away from the pore walls.

(2) A 'ternary phase' (stationary phase), constituted by the mixture of polymer solution and the gel matrix. Only a little fraction of the crosslinked polymer (gel matrix) is solvated by the solvent taking part in the separation process.

Throughout the text, the following nomenclature will be used to define the composition in both phases:

ϕ_{i0} ($i=1,2$): the volume fraction of the component i in the binary phase ($\phi_{10}+\phi_{20}=1$).

ϕ_i ($i=1,2,3$): the volume fraction of the component i in the ternary phase ($\phi_1+\phi_2+\phi_3=1$).

u_i ($i=1,2$): the volume fraction of the polymer solution (components 1 and 2) in the ternary phase, $u_i=\phi_i/(1-\phi_3)$.

The Flory–Huggins (F–H) expression for the Gibbs free energy of mixing, ΔG_M, for a system formed by two polymers and one solvent is[7]:

$$\Delta G_M/RT=\sum_{i=1}^{3} n_i \ln\phi_i+(g_{12}\phi_1\phi_2+g_{13}\phi_1\phi_3+g_{23}\phi_2\phi_3)\sum_{i=1}^{3} m_i n_i \quad (1)$$

and the corresponding expression, ΔG_M^b, for a system formed by a polymer and a solvent is

$$\Delta G_M^b/RT=n_1\ln\phi_{10}+n_2\ln\phi_{20}+n_1\phi_{20}g_{12}(\phi_{10}) \quad (2)$$

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where n_i is the number of moles of component i in the mixture, m_i the ratio between molar volumes of component i and component 1 (reference component) and g_{ij} the F–H interaction parameter which is related to the classical parameter, χ_{ij}, by

$$\chi_{ij}(\phi_j)=g_{ij}(\phi_j)-(1-\phi_j)(\mathrm{d}g_{ij}/\mathrm{d}\phi_j) \qquad (3)$$

at constant P and T.

In order to describe the equilibrium between both phases we can use the thermodynamics of polymer solutions writing[8]

$$(\partial G_u/\partial u_1)_{u_3}=(\partial \Delta G_M/\partial \phi_{10}) \qquad (4)$$

where G_u is the Gibbs function of mixing per unit volume of liquid in the ternary phase (or gel phase): $G_u=\Delta G_M/(V(1-\phi_3))$, V being the total volume. Recalling equations (1) and (2), we can write:

$$\begin{aligned}(\partial G_u/\partial u_1)_{u_3}=(RT/V_1)\{&\ln[u_1/(1+u_3)]+1-s\ln[u_2/(1+u_3)]\\ &-s+[1/(1+u_3)](u_2-u_1)g_{12}(u_1)\\ &+[1/(1+u_3)]u_1u_2(\mathrm{d}g_{12}/\mathrm{d}u_1)+\\ &+[1/(1+u_3)]u_3g_{13}(\phi_3)-[u_3/(1+u_3)]g_{23}(\phi_3)\}\end{aligned} \qquad (5)$$

and

$$\begin{aligned}(\partial\Delta G_M/\partial\phi_{10})=(RT/V_1)\{&\ln\phi_{10}+1-s\ln\phi_{20}-s+\\ &(\phi_{20}-\phi_{10})g_{12}(\phi_{10})+\phi_{10}\phi_{20}(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})\}\end{aligned} \qquad (6)$$

$s=V_1/V_2$, being the ratio between molar volumes of components 1 and 2. Substituting equations (5) and (6) into equation (4) and assuming that $g_{12}(u_1)\simeq g_{12}(\phi_{10})$ and $(\mathrm{d}g_{12}/\mathrm{d}u_1)\simeq(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})$[9] we arrive at

$$\begin{aligned}\ln(\phi_2/\phi_{20})=-m_2\phi_3\{&\phi_3^{-1}\ln(\phi_{10}/\phi_1)+g_{23}(\phi_3)-g_{13}(\phi_3)-\\ &g_{12}(\phi_{10})[1+2(\phi_2-\phi_{20})/\phi_3]-\{\phi_1\phi_2/[\phi_3(1-\phi_3)]\}\\ &(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})+\phi_{10}\phi_{20}/\phi_3)(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})\}\end{aligned} \qquad (7)$$

Equation (7) is similar to that obtained by other authors[10] excepting the two last terms of the right hand side, where they use the inadequate parameter χ.

Expanding $\ln(\phi_{10}/\phi_1)$ up to linear terms we can write $\phi_3^{-1}\ln(\phi_{10}/\phi_1)\simeq 1+(\phi_2-\phi_{20})/\phi_3$. Substituting this expression into equation (7), assuming that $\phi_{10}\phi_{20}\simeq\phi_1\phi_2$ and neglecting $\phi_2-\phi_{20}$ terms, we finally obtain

$$\begin{aligned}\ln(\phi_2/\phi_{20})=-m_2\phi_3\{&1+g_{23}(\phi_3)-g_{13}(\phi_3)-\\ &g_{12}(\phi_{10})-[\phi_{10}\phi_{20}/(1-\phi_3)(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})\}\end{aligned} \qquad (8)$$

Alternatively, when there are secondary mechanisms in the g.p.c. separation process, the retention volume of a solute polymer is given[2–4] by:

$$V_R=V_0+K_Dk_pV_i \qquad (9)$$

where V_0 is the interstitial or void volume, V_i is the total volume of solvent within the gel, K_D is the distribution coefficient for steric exclusion and k_p is the distribution coefficient for solute–gel interactions.

For k_p evaluation, Dawkins and Hemming proposed the expression

$$(V_R-V_0)/k_p=V_i(-A\log M[\eta]+B) \qquad (10)$$

in which it was assumed that the hydrodynamic volume is the size parameter determining the steric exclusion separation (A and B are constants). A plot of equation (10) as $\log M[\eta]$ *versus* the left hand side will give a universal calibration when solutes are separated solely by steric exclusion, $k_p=1$, or when solutes are separated both by steric exclusion and secondary mechanisms (partition and adsorption), $k_p>1$.

The quotient ϕ_2/ϕ_{20} in equation (8) is the partition coefficient k_p, thus we can write

$$\begin{aligned}\ln k_p=-m_2\phi_3\{&1+g_{23}(\phi_3)-g_{13}(\phi_3)-g_{12}(\phi_{10})-\\ &(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})[\phi_{10}\phi_{20}/(1-\phi_3)]\}\end{aligned} \qquad (11)$$

An equation similar to this, differing only in the last term, has already been derived by Horta *et al.*[5]

Since the partition coefficient, k_p, is evidently related to the sorption of the solute polymer onto the gel (or to the incompatibility between solute polymer and gel) it would be interesting to relate k_p to the preferential sorption coefficient, λ. The expression for λ at same conditions (finite ϕ_3) is[11]

$$\lambda(u_1,\phi_3)=\bar{v}_3A_1+\phi_3\bar{v}_3A_2 \qquad (12)$$

where $\bar{v}_3$ is the specific partial volume of polymer which constitutes the gel matrix, $A_1=-M_{13}/M_{11}$ and $A_2=-(A_1^2M_{111}+2A_1M_{113}+M_{133})/2M_{11}$, being

$$M_{ij}=\lim_{u_3\to 0}(\partial^2G_u/\partial u_i\partial u_j)_{u_3} \quad \text{and}$$

$$M_{ijk}=\lim_{u_3\to 0}(\partial^3G_u/\partial u_i\partial u_j\partial u_k)_{u_3}$$

Carrying out the calculations for M_{ij} and M_{ijk} we obtain

$$\begin{aligned}(V_1/RT)M_{13}=s-1+g_{13}^{\circ}-g_{23}^{\circ}-(\phi_{20}-\phi_{10})g_{12}(\phi_{10})\\ -\phi_{10}\phi_{20}(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})\end{aligned} \qquad (13)$$

$$\begin{aligned}(V_1/RT)M_{11}=1/\phi_{10}+s/\phi_{20}-2g_{12}(\phi_{10})+\\ 2(\phi_{20}-\phi_{10})(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})+\phi_{10}\phi_{20}(\mathrm{d}^2g_{12}/\mathrm{d}\phi_{10}^2)\end{aligned} \qquad (14)$$

$$\begin{aligned}(V_1/RT)M_{111}=-(1+s)-6(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})\\ +3(\phi_{20}-\phi_{10})\mathrm{d}^2g_{12}/\mathrm{d}\phi_{10}^2)\end{aligned} \qquad (15)$$

$$\begin{aligned}(V_1/RT)M_{113}=2g_{12}(\phi_{10})-2(\phi_{20}-\phi_{10})(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})-\\ \phi_{10}\phi_{20}(\mathrm{d}^2g_{12}/\mathrm{d}\phi_{10}^2)\end{aligned} \qquad (16)$$

and

$$(V_1/RT)M_{133}=1-s+2(\phi_{20}-\phi_{10})g_{12}(\phi_{10})-2g_{13}^{\circ}+2g_{23}^{\circ}, \qquad (17)$$

where g_{ij}° are the interaction parameters at infinite dilution. Since the selective or preferential sorption of solute polymer (or solvent) onto the gel is irrespectively quantified by equations (11) and (12), both equations must be related.

RESULTS AND DISCUSSION

As has been already mentioned the partition coefficients, k_p, have relative characters and their experimental evaluation requires a reference system in which $k_p = 1$ (steric exclusion). From a thermodynamic point of view, equation (11) and (12) can serve to define a reference state in which the polymers are separated solely by steric exclusion.

At sufficiently low ϕ_3 values, equation (11) can be simplified to

$$\ln k_p \simeq -m_2\phi_3(1 + g_{23}^\circ - g_{13}^\circ - g_{12}^\circ) \qquad (18)$$

because at these conditions $g_{ij} = g_{ij}^\circ + \phi_j(\mathrm{d}g_{ij}/\mathrm{d}\phi_j) \simeq g_{ij}^\circ$ when $\phi_j \rightarrow 0$. Furthermore, in equation (18) it has been assumed that $\phi_2 \simeq \phi_{20} \simeq 0$, as is usual in chromatographic experiments.

Equation (18) is equal to that deduced by Horta *et al.*[5] (excepting the parameters g_{ij} which, in our case, are expressed at infinite dilution) and it is also equivalent to the expression obtained by Lecourtier *et al.*[12].

$$\ln k_p = X_2\{\ln(1-\phi_3) + \phi_3(\chi_{23} - \chi_{13} - \chi_{12})\} \simeq -X_2\phi_3(1 + \chi_{23} - \chi_{13} - \chi_{12}) \qquad (19)$$

The k_p value predicted by equation (19) is qualitatively similar to that given in equation (18) as long as $m_2 = V_2/V_1$ is proportional to the degree of polymerization X_2. Nevertheless, equation (18) is more general than equation (19) because of the dependence of the g_{ij} parameters on polymer concentration[9].

The equation for λ, when $\phi_3 \rightarrow 0$, is

$$\lambda(u_1) = -\bar{v}_3\{[-1 - g_{23}^\circ + g_{13}^\circ + g_{12}^\circ]/[1 - 2g_{12}^\circ - 2(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})]\} \qquad (20)$$

where s has been neglected ($s = V_1/V_2$ and $V_2 \gg V_1$).

On the other hand, the g_{23}° values can be calculated from[13,14]

$$g_{23}(\phi_3) = [1/(1-\phi_3)]\int_{\phi_3}^{1} \chi_{23}(\phi_3)\mathrm{d}\phi_3 \qquad (21)$$

considering the variation of χ_{23} with ϕ_3

$$\chi_{23}(\phi_3) = \chi_{23}^\circ + \chi_{23}'\phi_3 + \chi_{23}''\phi_3^2 + \dots \qquad (22)$$

we can write

$$g_{23}(\phi_3) = (\chi_{23}^\circ + \chi_{23}'/2 + \chi_{23}''/3 + \dots) + (\chi_{23}'/2 + \chi_{23}''/3 + \dots)\phi_3 = g_{23}^\circ + g_{23}'\phi_3 + \dots \qquad (23)$$

and then

$$g_{23}^\circ = \chi_{23}^\circ + \chi_{23}'/2 + \chi_{23}''/3 + \dots \qquad (24)$$

The values of interaction parameters between two polymers, χ_{23}°, are usually low and they decrease as molecular weight increases[7,15]. Taking into account that the values of the χ_{23}', χ_{23}'', ... coefficients are also low and that the gel matrix is a crosslinked polystyrene of very high molecular weight, g_{23}° values can be neglected and equations (18) and (20) can be respectively written as

$$\ln k_p \simeq -m_2\phi_3(1 - g_{13}^\circ - g_{12}^\circ) \qquad (25)$$

$$\lambda(u_1) = -\bar{v}_3\{[-1 + g_{13}^\circ + g_{12}^\circ]/[1 - 2g_{12}^\circ - 2(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})]\} \qquad (26)$$

Negative values of λ will indicate preferential sorption of solute polymer (component 2) onto the gel matrix (component 3) and can be interpreted as follows: the macromolecules are 'dissolved' within the 'gel phase' (the macromolecules penetrate inside the grains). The above result is in good agreement with those reached by other authors[12,16]. In these conditions $k_p > 1$ and $\ln k_p > 0$. For usual k_p values, that is $1 < k_p < 3$[2-4], and regarding equation (25), two facts arise:

(1) since m_2 values are high ($m_2 = V_2/V_1$) the corresponding ϕ_3 values must be very low as previously mentioned, and
(2) the $(1 - g_{13}^\circ - g_{12}^\circ)$ value is negative.

Therefore, in the cyclohexane (CH)/polystyrene (PS)/Styragel (ST) system at 35°C, $k_p > 1$[2-4] with a reference system formed by a good solvent for PS/PS/ST. In the former system $g_{13}^\circ \simeq g_{12}^\circ \simeq 0.705$[17] and then $(1 - g_{13}^\circ - g_{12}^\circ) < 0$. Moreover, λ will be negative because $-(\mathrm{d}g_{12}/\mathrm{d}\phi_{10}) \simeq -(\mathrm{d}g_{12}/\mathrm{d}\phi_1) = (\mathrm{d}g_{12}/\mathrm{d}\phi_2) \simeq 0.206$[17] and $[1 - 2g_{12}^\circ - 2(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})] > 0$.

It is interesting to note that the compatibility between the polymers is a direct consequence of the incompatibility between both polymers and the solvent (CH at 35°C is a 'theta' solvent for solute polymer and for the gel matrix polymer).

Contrary to the above is the case of incompatibility between solute polymer and gel matrix. A system satisfying the conditions $0 < k_p < 1$ and $\ln k_p < 0$ and $(1 - g_{13}^\circ - g_{12}^\circ) > 0$ is the benzene (BZ)/PS/ST at 25°C, in spite of the polymers seeming to be compatible. For this system $g_{13}^\circ \simeq g_{12}^\circ \simeq 0.455$[9] and $(1 - g_{13}^\circ - g_{12}^\circ) > 0$. These values together with $-(\mathrm{d}g_{12}/\mathrm{d}\phi_{10}) \simeq -(\mathrm{d}g_{12}/\mathrm{d}\phi_1) = (\mathrm{d}g_{12}/\mathrm{d}\phi_2) \simeq 0$[9] lead to $[1 - 2g_{12}^\circ - 2(\mathrm{d}g_{12}/\mathrm{d}\phi_{10})] > 0$ and $\lambda > 0$ (the solvent is preferentially sorbed into the gel matrix). For this case, although λ values are positive, in absolute terms they are smaller than the above λ negative values.

In the light of the above examples it is clear that the compatibility (or incompatibility) between two polymers must be studied in relation to both polymers, depending on the solvent used. This aspect can be related to the absence of the g_{23}° parameter in equations (25) and (26).

At this point, an ideal reference system can be defined as a system in which $(1 - g_{13}^\circ - g_{12}^\circ) = 0$, with λ also being equal to zero. The former condition is equivalent to that deduced by Horta *et al.*[5].

Equations (25) and (26) can be applied to chromatographic studies of ternary systems comprised of solvent(1)/polymeric solute(2)/gel matrix(3) if k_p values and $g_{12}(\phi_2)$ and $g_{13}(\phi_3)$ values were known.

In order to carry out the calculations equation (25) can be written as

$$\ln k_{\rm p} = -(V_2/V_1)\phi_3[1-(g^\circ_{13}+g'_{13}\phi_3+g''_{13}\phi_3^2+\ldots)-g^\circ_{12}] \tag{27}$$

that is to say, ϕ_3 is low but not negligible and $\phi_2 \simeq 0$ as is usual in chromatographic experiments. Under these conditions, if the ϕ_3 values were known for a system, λ values can be evaluated through equation (12).

Experimentally, the λ variation with molecular weight of solvated polymer is given by[11,18]

$$\lambda M^{1/2} = \lambda_\infty M^{1/2} + A \tag{28}$$

A suitable method of correlating the evaluated λ with the above expression consists of a new definition of the ternary system as solvent(1)/gel matrix(2)/solute polymer(3). Now, $\phi_3 \simeq 0$ (volume fraction of solvated polymer) and ϕ_2 is equivalent to ϕ_3 in equation (12). With these new conditions the expression for λ is:

$$\begin{aligned}\lambda(u_1,\phi_3) \simeq \lambda(u_1) &= -\bar{v}_3(M_{13}/M_{11})\\ &= -\bar{v}_3[s-1+g^\circ_{13}-g^\circ_{23}-(\phi_2-\phi_1)g_{12}(\phi_1)\\ &\quad -\phi_1\phi_2({\rm d}g_{12}/{\rm d}\phi_1)]/[1/\phi_1+s/\phi_2-2g_{12}(\phi_1)\\ &\quad +2(\phi_2-\phi_1)({\rm d}g_{12}/{\rm d}\phi_1)+\phi_1\phi_2({\rm d}^2g_{12}/{\rm d}\phi_1^2)]\end{aligned} \tag{29}$$

Considering that $g_{12}(\phi_2)$ can be written as $g_{12}(\phi_2) = g^\circ_{12}+g'_{12}\phi_2+g''_{12}\phi_2^2 = g^\circ_{12}+g'_{12}(1-\phi_1)+g''_{12}(1-\phi_1)^2$ the derivatives will be given by

$$({\rm d}g_{12}/{\rm d}\phi_1) \simeq ({\rm d}g_{12}/{\rm d}\phi_{10}) = -g'_{12}-2g''_{12}\phi_2 \tag{30}$$

$$({\rm d}^2g_{12}/{\rm d}\phi_1^2) \simeq ({\rm d}^2g_{12}/{\rm d}\phi_{10}^2) = 2g''_{12} \tag{31}$$

Substitution of equations (30) and (31) into equation (29) yields

$$\begin{aligned}\lambda(u_1) = -\bar{v}_3[s-1+g^\circ_{13}-(\phi_2-\phi_1)(g^\circ_{12}+g'_{12}\phi_2+g''_{12}\phi_2^2)+\\ \phi_1\phi_2(g'_{12}+2g''_{12}\phi_2)]/[1/\phi_1+s/\phi_2-2(g^\circ_{12}+g'_{12}\phi_2+\\ g''_{12}\phi_2^2)-2(\phi_2-\phi_1)(g'_{12}+2g''_{12}\phi_2)+2\phi_1\phi_2g''_{12}]\end{aligned} \tag{32}$$

Numerical calculations in this paper have been carried out from literature data as follows:

(1) Considering the ternary system as solvent(1)/solute polymer(2)/gel matrix(3), ϕ_3 values have been calculated through equation (27) from $k_{\rm p}$ experimental values obtained via g.p.c.

(2) Taking into account the new definition of the ternary system, that is, solvent(1)/gel matrix(2)/solute polymer(3), $\lambda(u_1)$ values have been calculated through equation (32) from ϕ_2 values (that are equivalent to above ϕ_3).

(3) Equation (28) has been finally applied, with calculated λ values, to each system.

Figure 1 is a plot of log $M[\eta]$ *versus* $(V_{\rm R}-V_0)/k_{\rm p}$ for the systems tetrahydrofuran (THF)/PS/μStyragel (μST) at 25°C and CH/PS/μST at 35°C. *Table 1* summarizes the results for the latter system. As can be seen, the higher the $k_{\rm p}$ values the higher are the molecular weights of the solute polymer. This behaviour agrees qualitatively with that predicted by equation (25). With the g°_{13} and g°_{12} values given at the bottom of the table the expression in brackets in equation (25) is negative and so, since m_2 is proportional to the degree of polymerization, predicted $k_{\rm p}$ values are higher as the molecular weight of solute polymer increases. ϕ_3 values, on the contrary, decrease as molecular weight increases, as *Table 1* shows.

On the other hand, negative values of λ indicate a large sorption of the polymer by the gel matrix. The higher the λ values the higher the molecular weight of solvated polymer, this trend being experimentally observed in ternary solvent(1)/solvent(2)/polymer(3) systems[19]. Finally, *Table 1* shows the correlation coefficient for the representation $\lambda M^{1/2}$ *versus* $M^{1/2}$ (equation (28)) this

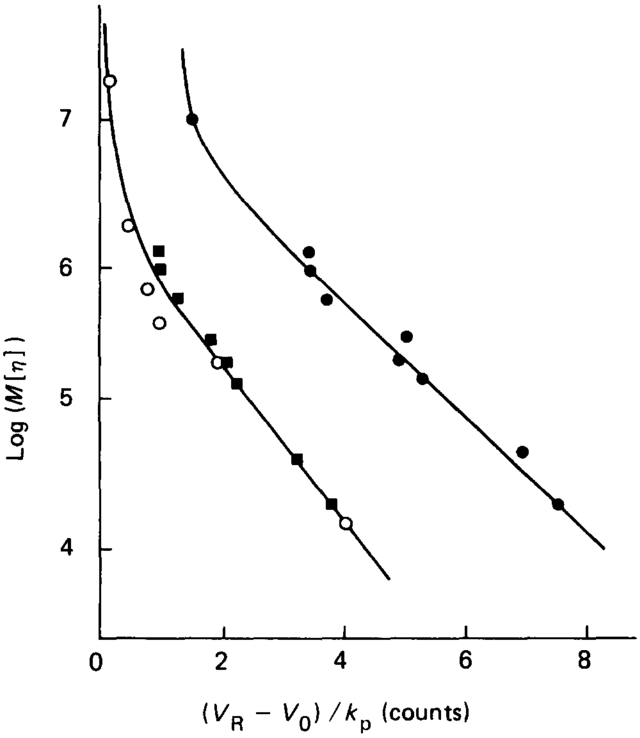

Figure 1 Universal calibration plot for CH/μST/PS system at 35°C (●), $k_{\rm p}=1$, THF/μST/PS at 25°C (○), $k_{\rm p}=1$, and CH/μST/PS at 35°C (■) with $k_{\rm p}$ values for each molecular weight given in *Table 1*. Experimental data from ref. 6

Table 1 Experimental $k_{\rm p}$, ϕ_3 (or ϕ_2) and λ values for CH/μST/PS system at 35°C. Reference system: THF/μST/PS at 25°C[6]

$k_{\rm p}$	$M_{\rm w}$	$\phi_3=\phi_2{}^a$	λ (ml g^{-1})^b
2.00	3600	0.05385	−0.582
2.19	6000	0.03685	−0.673
2.40	13000	0.01916	−0.774
2.57	15000	0.01792	−0.835
2.80	21000	0.01399	−0.917
2.84	35000	0.00853	−0.940
2.87	49000	0.00616	−0.923
2.90	60000	0.00508	−0.966

Necessary data for calculations:
g°_{13} (equation (27)) $= g^\circ_{12}$ (equation (32)) $= 0.705$.
g'_{13} (equation (27)) $= g'_{12}$ (equation (32)) $= 0.206$.
g''_{13} (equation (27)) $= g''_{12}$ (equation (32)) $= 0.052$.
g°_{12} (equation (27)) $= g^\circ_{13}$ (equation (32)) $= 0.705$.
$V_1 = 108.74$ ml mol^{-1}; $V_2 = M_{\rm w} = 0.923$ ml mol^{-1}; $\bar{v}_3 = 0.923$ ml g^{-1}
[a] ϕ_3 (equation (27)) or ϕ_2 (equation (32)) values
[b] λ (equation (32)) values
Results obtained through equation (28): $A = 32.616$; $\lambda_\infty = -1.105$
Correlation coefficient $= 0.9992$

value indicating that calculated λ values follow the same laws with respect to molecular weight as in the case of ternary solvent(1)/solvent(2)/polymer(3) systems. Moreover, as λ values directly depend on ϕ_2 (equation (29)) or ϕ_3 (equation (27)), the above result confirms that ϕ_3 is not a constant as was previously described[20] but depends on molecular weight of solvated polymer and this variation can affect k_p values as do m_2 values (g_{ij} values scarcely vary with molecular weight[13,21,22]).

Table 2 Experimental k_p, ϕ_3 (or ϕ_2) and λ values for CH/ST (10^6, 10^5, 10^4 and 10^3 Å)/PS system at 35°C. Reference system: CH/ST (10^6, 10^5, 10^4 and 10^3 Å)/PDMS, PI at 35°C[2-4]

k_p	M_w	$\phi_3=\phi_2{}^a$	λ (ml g^{-1})^b
1.45	1800	0.05762	−0.336
	3700	0.02845	−0.339
	10300	0.01031	−0.341
	19800	0.00537	−0.341
	51000	0.00209	−0.342
	98200	0.00109	−0.343
	160000	0.00067	−0.342

Necessary data for calculations: g°_{ij}, g'_{ij}, g''_{ij}, V_1, V_2 and $\bar{v}_3$ from *Table 1*; ^{a} and ^{b} as in *Table 1*

Results obtained through equation (28): $A=0.250$; $\lambda_\infty=-0.343$

Correlation coefficient: 0.999996

Table 3 Experimental k_p, ϕ_3 (or ϕ_2) and λ values for CH/ST(10^4 Å)/PS system at 35°C. Reference system: CH/ST(10^4 Å)/PDMS, PI at 35°C[2-4]

k_p	M_w	$\phi_3=\phi_2{}^a$	λ (ml g^{-1})^b
1.60	1800	0.07235	−0.404
	3700	0.03585	−0.419
	10300	0.01303	−0.428
	19800	0.00680	−0.430
	51000	0.00265	−0.433
	98200	0.00137	−0.431
	160000	8.43×10^{-4}	−0.432
	411000	3.28×10^{-4}	−0.432
	498000	2.71×10^{-4}	−0.432
	670000	2.01×10^{-4}	−0.432
	867000	1.56×10^{-4}	−0.433

Necessary data for calculations: g°_{ij}, g'_{ij}, g''_{ij}, V_1, V_2 and $\bar{v}_3$ from *Table 1*; ^{a} and ^{b} as in *Table 1*

Results obtained through equation (28): $A=0.717$; $\lambda_\infty=-0.433$

Correlation coefficient: 0.999995

Table 4 Experimental k_p, ϕ_3 (or ϕ_2) and λ values for CH/ST(10^3 Å)/PS system at 35°C. Reference system: CH/ST(10^3 Å)/PDMS, PI at 35°C[2-4]

k_p	M_w	$\phi_3=\phi_2{}^a$	λ (ml g^{-1})^b
4.50	1800	0.21550	−0.620
	3700	0.11050	−0.987
	10300	0.04110	−1.233
	19800	0.02159	−1.302
	51000	0.00844	−1.349
	98200	0.00439	−1.362
	160000	0.00270	−1.370
	411000	0.00105	−1.373
	498000	8.67×10^{-4}	−1.374
	670000	6.44×10^{-4}	−1.374
	867000	4.98×10^{-4}	−1.375

Necessary data for calculations: g°_{ij}, g'_{ij}, g''_{ij}, V_1, V_2 and $\bar{v}_3$ from *Table 1*; ^{a} and ^{b} as in *Table 1*

Results obtained through equation (28): $A=18{,}885$; $\lambda_\infty=-1.401$

Correlation coefficient: 0.99990

Analogous results to the above results are shown in *Table 2* for the CH/ST (10^6, 10^5, 10^4 and 10^3 Å)/PS system[2-4] (according to the new nomenclature adopted for the λ evaluation in equation (32)). For this system $k_p=1.45$[2-4] independently of molecular weight. This result deserves some comment; if m_2 variation is compensated by the ϕ_3 variation then equation (25) will yield a k_p value irrespective of molecular weight and so, in those systems in which k_p is a constant, large variations in ϕ_3 with molecular weight can be expected. As can be seen in *Table 2* the variation of ϕ_3 with molecular weight is greater than that in *Table 1* for the same molecular weight range.

Tables 3 and *4* show ϕ_3 and λ values obtained from literature data[2-4] for CH/ST (10^4 Å)/PS and CH/ST (10^3 Å)/PS systems at 35°C. The k_p values used were 1.6 for the former system and 4.5 for the latter one, and the reference system was the same as in *Table 2*. g_{ij} values are given at the bottom of the table. Similar comments to those made in *Table 1* can be applied to results collected in these tables, the only difference that stands out is that for equivalent molecular weights, the absolute λ values are lower than those in *Table 1*. This aspect can be related to the lower specific surface of ST with respect to that of μST. A good linearity is achieved in both cases when equation (28) is applied, as deduced from the correlation coefficients.

ϕ_3 and λ values calculated for *trans*-decalin (TD)/ST/PS system at 25°C, 60°C and 100°C are shown in *Tables 6*, *7* and *8*, respectively, with CH/ST/poly(dimethylsiloxane)(PDMS) as the reference system under the same chromatographic conditions. g_{ij} values are necessary to apply equations (27) and (32), but they are scarce in the literature[9]. To overcome this difficulty the following procedure has been used to evaluate these values. From intrinsic viscosities, $[\eta]$, and through the Stockmayer–Fixmann equation

$$[\eta]/M^{1/2}=K_\theta+0.51\phi_0BM^{1/2} \qquad (33)$$

K_θ and B values can be calculated. *Table 5* shows K_θ and B values obtained for three temperatures using $[\eta]$ in ml g^{-1} and $\phi_0\simeq2.5\times10^{23}$. B is related to the parameter χ° (Flory–Huggins interaction parameter at infinite dilution) through the expression

$$B=(2\bar{v}^2/N_0V_s)(0.5-\chi^\circ) \qquad (34)$$

where $\bar{v}$ is the specific partial volume of the polymer, N_0 Avogadro's number and V_s the molar volume of solvent. χ° values calculated through equation (34) are gathered in

Table 5 χ°_{13} (equation (34)), g°_{13} (equation (35)) and g'_{13} (equation (36)) values calculated for various systems

System	$K_\theta\times10^2$	$B\times10^{28}$	V_1 (ml mol^{-1})	χ°_{13}	g°_{13}	g°_{12}	g'_{13}
TD/ST/PS (25°C)	7.296	0.535	157.3	0.497	0.663	0.663	0.166
TD/ST/PS (60°C)	8.350	5.837	167.4	0.465	0.621	0.621	0.155
TD/ST/PS (100°C)	7.470	6.953	176.8	0.457	0.609	0.609	0.152
CH/ST/PS (45°C)	7.584	2.569	110.8	0.490	0.653	0.653	0.163

Table 6 Experimental k_p, ϕ_3 (or ϕ_2) and λ values for TD/ST/PS system at 25°C. Reference system: TD/ST/PDMS at 25°C[2–4]

k_p	M_w	$\phi_3=\phi_2$[a]	λ (ml g^{-1})[b]
1.25	1800	5.797×10^{-2}	−0.269
	3700	2.973×10^{-2}	−0.281
	10300	1.108×10^{-2}	−0.290
	19800	5.823×10^{-3}	−0.293
	51000	2.277×10^{-3}	−0.295
	98200	1.185×10^{-3}	−0.295
	160000	7.28×10^{-4}	−0.296
	498000	2.34×10^{-4}	−0.296
	867000	1.35×10^{-4}	−0.297
	1900000	6.14×10^{-4}	−0.296

Necessary data for calculations:
g°_{13} (equation (27)) $=g^\circ_{12}$ (equation (32)) $=0.663$
g'_{13} (equation (27)) $=g'_{13}$ (equation (32)) $=0.166$
g''_{13} (equation (27)) $=g''_{13}$ (equation (32)) $=0$
g°_{12} (equation (27)) $=g^\circ_{13}$ (equation (32)) $=0.663$
V_1 from *Table 5*; V_2, $\bar{v}_3$ from *Table 1*; [a] and [b] as in *Table 1*
Results obtained through equation (28): $A=0.713$; $\lambda_\infty=-0.297$
Correlation coefficient = 0.999996

Table 7 Experimental k_p, ϕ_3 (or ϕ_2) and λ values for TD/ST/PS system at 60°C. Reference system: TD/ST/PDMS at 60°C[2–4]

k_p	M_w	$\phi_3=\phi_2$[a]	λ (ml g^{-1})[b]
1.20	1800	6.506×10^{-2}	−0.209
	3700	3.397×10^{-2}	−0.221
	10300	1.284×10^{-2}	−0.232
	19800	6.784×10^{-3}	−0.236
	51000	2.662×10^{-3}	−0.238
	98200	1.378×10^{-3}	−0.239
	160000	8.52×10^{-4}	−0.239
	498000	2.74×10^{-4}	−0.240
	867000	1.57×10^{-4}	−0.239
	1900000	7.2×10^{-5}	−0.240

Necessary data for calculations:
g°_{13} (equation (27)) $=g^\circ_{12}$ (equation (32)) $=0.621$
g'_{13} (equation (27)) $=g'_{13}$ (equation (32)) $=0.155$
g''_{13} (equation (27)) $=g''_{13}$ (equation (32)) $=0$
g°_{12} (equation (27)) $=g^\circ_{13}$ (equation (32)) $=0.621$
V_1 from *Table 5*; V_2, $\bar{v}_3$ from *Table 1*; [a] and [b] as in *Table 1*
Results obtained through equation (28): $A=0.882$; $\lambda_\infty=-0.241$
Correlation coefficient = 0.999994

Table 5. Once the χ° parameters are known, g°_{13} can be evaluated from[23]

$$\chi^\circ_{13}=[1-(2/Z)]g^\circ_{13} \tag{35}$$

where Z is the coordination number of the network. A value of $Z=8$ [24] has been used. $g^\circ_{13}=g^\circ_{12}$ because both the solute and the gel are the same polymer and taking into account the equation of Koningsveld *et al.*[13,17,21,22] we can write

$$g'_{12}=g'_{13}=(\mathrm{d}g_{13}/\mathrm{d}\phi_3)_{\phi_3\to0}=g^\circ_{13}-\chi^\circ_{13} \tag{36}$$

Table 5 shows g°_{13}, g°_{12} and g'_{13} values for each system. There is no information concerning g''_{13} values in the bibliography, however, they always are multiplied by ϕ_j^2 and as ϕ_j is very low, their values can be neglected in any calculations.

λ values gathered in *Tables 6*, *7* and *8* completely fulfil equation (28) as the correlation coefficients indicate. Also it can be noted that, for the same molecular weight, the λ values decrease when the temperature is raised, that is to say the secondary mechanisms are lower as temperature is higher.

Finally, in *Table 9* results for the CH/ST(10^3 Å)/PS system at 45°C[2–4] are shown, $k_p=2$ with PDMS as the reference system. g_{ij} values necessary for application of equations (27) and (32) are given in *Table 5*. As can be seen λ values follow equation (28) well as the correlation coeficients indicate. If results of *Table 9* are compared with those of *Table 4* (the same system but at 35°C) k_p values fall from 4.5 to 2.0 and λ diminishes in absolute value. This result again confirms that the lower the λ values the lower the importance of the secondary mechanisms.

Throughout the tables, it can be observed that k_p is not always a constant. As other authors confirm[24], k_p values may vary with molecular weight. As has been already mentioned k_p and λ must be related. In this way, we have found a variation for k_p similar to that of equation (32) for λ. That is to say, $k_pM^{1/2}$ vs. $M^{1/2}$ is a linear correlation. The study of this variation will be subject of a subsequent paper.

Table 8 Experimental k_p, ϕ_3 (or ϕ_2) and λ values for TD/ST/PS system at 100°C. Reference system: TD/ST/PDMS at 100°C[2–4]

k_p	M_w	$\phi_3=\phi_2$[a]	λ (ml g^{-1})[b]
1.10	1800	4.168×10^{-2}	−0.136
	3700	2.136×10^{-2}	−0.134
	10300	7.955×10^{-3}	−0.134
	19800	4.181×10^{-3}	−0.135
	51000	1.635×10^{-3}	−0.135
	98200	8.51×10^{-4}	−0.135
	160000	5.23×10^{-4}	−0.135
	498000	1.68×10^{-4}	−0.135
	867000	9.7×10^{-5}	−0.135
	1900000	4.4×10^{-5}	−0.135

Necessary data for calculations:
g°_{13} (equation (27)) $=g^\circ_{12}$ (equation (32)) $=0.609$
g'_{13} (equation (27)) $=g'_{13}$ (equation (32)) $=0.152$
g''_{13} (equation (27)) $=g''_{13}$ (equation (32)) $=0$
g°_{12} (equation (27)) $=g^\circ_{13}$ (equation (32)) $=0.609$
V_1 from *Table 5*; V_2, $\bar{v}_3$ from *Table 1*; [a] and [b] as in *Table 1*
Results obtained through equation (28): $A=-0.020$; $\lambda_\infty=-0.135$
Correlation coefficient = 0.999994

Table 9 Experimental k_p, ϕ_3 (or ϕ_2) and λ values for CH/ST/PS system at 45°C. Reference system: CH/ST/PDMS at 45°C[2–4]

k_p	M_w	$\phi_3=\phi_2$[a]	λ (ml g^{-1})[b]
2.00	1800	1.202×10^{-1}	−0.390
	3700	6.455×10^{-2}	−0.485
	10300	2.504×10^{-2}	−0.565
	19800	1.334×10^{-2}	−0.591
	51000	5.268×10^{-3}	−0.610
	98200	2.751×10^{-3}	−0.616
	160000	1.692×10^{-3}	−0.619
	498000	5.45×10^{-4}	−0.621
	867000	3.13×10^{-4}	−0.622
	1900000	1.43×10^{-4}	−0.622

Necessary data for calculations:
g°_{13} (equation (27)) $=g^\circ_{12}$ (equation (32)) $=0.653$
g'_{13} (equation (27)) $=g'_{13}$ (equation (32)) $=0.163$
g''_{13} (equation (27)) $=g''_{13}$ (equation (32)) $=0$
g°_{12} (equation (27)) $=g^\circ_{13}$ (equation (32)) $=0.653$
V_1 from *Table 5*; V_2, $\bar{v}_3$ from *Table 1*; [a] and [b] as in *Table 1*
Results obtained through equation (28): $A=6.168$; $\lambda_\infty=-0.628$
Correlation coefficient = 0.99997

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