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## CORRELATIONS BETWEEN RETENTION VOLUMES AND THE INTERFACIAL TENSION OF THE TWO PHASES IN LIQUID-LIQUID CHROMATOGRAPHY

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### SUMMARY

It is shown that the interfacial tension between the mobile and the stationary phases reflects the partition properties of the two phases, and this can be taken as a criteria of choice of the systems used in liquid-liquid chromatography.

A semi-theoretical treatment shows that the Gibbs free energy of partition of the solute between the two phases is quasi-proportional to the surface tension, provided that the solubility of each phase in the other is small. Such behaviour is observed with organic solvent-water systems for solvents that give a surface tension greater than 20-25 dynes/cm. As mixtures of mobile phases behave in the same way, the retention times in programmed gradient analysis can be predicted.

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### INTRODUCTION

Since the early days of chromatography, chemists have tried to arrange stationary phases in order for the purpose of predicting the retention times of the eluted species. The fact that a word as vague as "polarity" had to be used in order to characterize the solvents reflects our inability to handle such a difficult problem. Nevertheless, the concept of polarity has been useful and has given rise to many publications, which have been very well summarized in a recent review by Keller<sup>1</sup>. Many correlations and scales have been proposed but it now seems to be accepted that the behaviour of a solvent depends so much on the solute with which it is associated that no single parameter can characterize the chromatographic system sufficiently accurately.

For the above reason, the extended solubility parameters theory, developed by Keller *et al.*<sup>2</sup> and by Snyder *et al.*<sup>3</sup>, is certainly a large step towards an acceptable answer, whereas factor analysis of the experimental results, as carried out by Weiner and co-workers<sup>4,5</sup>, appears to be the most realistic way of approaching the problem. The matter is still open, however, as the best that can be achieved from those theories is the prediction of the order of magnitude of the retention time in gas-liquid chromatography (GLC). Hence it is not surprising that the situation is much more uncertain

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in liquid-liquid chromatography (LLC), where the choice of the system is more challenging than in GLC, particularly when two solvents are mixed in various proportions, as in the elution gradient technique.

In a case where classical theories hardly hold, it might be interesting to investigate in more detail such relationships as that which can exist between the interfacial tension of the two phases and the partition properties of solutes between these two phases; the present paper is devoted to this matter.

In fact, this idea is not new and, as early as 1960, Vignes<sup>6</sup> published experimental results that showed a quasi-linear variation of the logarithm of the thermodynamic partition constant with the interfacial tension of the two solvents. Surprisingly, his work does not seem to have arisen much interest among chromatographers and, as the problem still seems to be of interest, in this first paper we report further investigations into the matter.

## THEORETICAL

Although the theory of interfacial phenomena is not yet well developed, we first wish to give some of the reasons that make us feel that the interfacial tension is a convenient variable for predicting the retention times of solutes in LLC. In order to make the matter simpler, we shall consider only the two extreme cases where the retention processes are either pure partition or pure adsorption.

In partition chromatography, the retention volume is assumed to be related to the volume of stationary phase through the partition coefficient,  $K_R$ , via the classical equation

$$V_R = K_R V_l \quad (1)$$

where<sup>7</sup>

$$K_{Rl} = \frac{X_i^S V_0^M}{X_i^M V_0^S} = \frac{\gamma_i^{M,\infty} V_0^M}{\gamma_i^{S,\infty} V_0^S} \quad (2)$$

In eqn. 2, the superscripts  $S$  and  $M$  indicate the stationary and the mobile phases, respectively,  $V_0$  is the molar volume,  $X_i$  is the mole fraction of the compound  $i$  and  $\gamma_i^\infty$  its activity coefficient at infinite dilution in either the  $M$  or  $S$  phase. The ratio  $X_i^S / X_i^M = \gamma_i^{M,\infty} / \gamma_i^{S,\infty}$  is called the thermodynamic partition coefficient.

In adsorption chromatography, the retention volume is the product of the adsorption coefficient,  $K_A$ , multiplied by the total surface area,  $A_L$ , of the gas-liquid interface. By analogy with  $K_R$ ,  $K_A$  can be written as<sup>8</sup>

$$K_{Al} = \frac{X_i^L V_0^M}{X_i^M A_0^L} \quad (3)$$

where  $X_i^L$  is the mole fraction of the solute  $i$  in the surface layer and  $A_0^L$  the molar area of 1 mole of solution at the liquid-liquid interface.

The problem with which we are dealing is to find a relationship between both  $K_R$  and  $K_A$  and the interfacial tension. Besides an ideal solution, the simplest type of

solution is a regular solution, so we shall first examine a chromatographic system that involves this type of solution.

*Partition coefficients and interfacial tensions for regular solutions*

It is now recognized that the interfacial tension is directly related to the solubility of each liquid in the other<sup>9</sup>, and this very significant observation is at the basis of almost all of the molecular models of the interface between two liquids<sup>10</sup>. Such a relationship is, in fact, to be expected, as the same intermolecular forces are the main features that contribute both to the interfacial tension and to the mutual solubility of the two liquids. Hence we can expect to obtain at least a good qualitative description of this phenomenon by using the solubility parameter theory, although only dispersive forces would be taken into account. However, the use of the solubility parameter theory is limited to partition processes.

If the species used as mobile and stationary phases are referred to as 1 and 2, respectively, the interfacial tension between these two solvents is then related to the molar area,  $A$ , of the solution, and to the concentrations after equilibration of species 1 and 2 in the stationary phase ( $S$ , dilute solution of 1 in 2), in the mobile phase ( $M$ , dilute solution of 2 in 1) and in the interfacial layer ( $L$ ), through two sets of equations<sup>11</sup>:

$$\sigma_{S/M} A = RT \ln \frac{X_1^L}{X_1^S} + \alpha \left[ (X_2^L)^2 - (X_2^S)^2 \right] + \alpha_m \left[ (X_2^L - X_2^S)^2 + (X_2^L - X_2^M)^2 - 2 X_2^L (2 X_2^L - X_2^S - X_2^M) \right] \quad (4)$$

$$\sigma_{S/M} A = RT \ln \frac{X_2^L}{X_2^M} + \alpha \left[ (X_1^L)^2 - (X_1^S)^2 \right] + \alpha_m \left[ (X_1^L - X_1^S)^2 + (X_1^L - X_1^M)^2 + 2 X_1^L (2 X_1^L - X_1^S - X_1^M) \right] \quad (4a)$$

where

$$\alpha = RT \ln \gamma_1^{M,\infty} = RT \ln \gamma_2^{S,\infty} \quad (5)$$

and  $m$  is a constant, the value of which can be taken as 1/6.

As necessary when dealing with strictly regular solutions, the molar volumes of species 1 and 2 are assumed to be equal in the derivation of eqns. 4, 4a and 5.

In a chromatographic system, the mutual solubility of species 1 and 2 should be small, so that we can state that  $X_1^S \approx 1$  and  $X_2^M \approx 1$ . As this implies that both  $\gamma_1^S$  and  $\gamma_2^M \approx 1$  we can, by virtue of eqn. 2, write

$$X_1^M = \frac{1}{\gamma_1^{M,\infty}} \quad (6)$$

$$X_2^S = \frac{1}{\gamma_2^{S,\infty}} \quad (6a)$$

The activity coefficients that appear in eqns. 6 and 6a can then be calculated via the solubility parameters theory<sup>12</sup>:

$$\gamma_1^{M,\infty} = \exp \left[ \frac{V_0^1}{RT} (\delta_1 - \delta_2)^2 \right] \quad (7)$$

$$\gamma_2^{S,\infty} = \exp \left[ \frac{V_0^2}{RT} (\delta_2 - \delta_1)^2 \right] \quad (7a)$$

In the same way, we can also show that the partition coefficient of a solute 3 is given by

$$K = \frac{X_3^S}{X_3^M} = \frac{\exp [V_0^3/RT (\delta_3 - \delta_2)^2]}{\exp [V_0^3/RT (\delta_3 - \delta_1)^2]} \quad (8)$$

Next, we can estimate the molar area of the different species by considering that each molecule occupies a quasi-spherical cavity; then we can write

$$A_0^l = (V_0^l)^{1/3} N^{2/3} \quad (9)$$

where  $N$  is Avogadro's number.

By combining eqns. 4–9, we can calculate the logarithm of the partition coefficient of solute 3, and the surface tension between the two phases, as two functions of the solubility parameters  $\delta_1$ ,  $\delta_2$  and  $\delta_3$ .

Results corresponding to the case when all three compounds have a molar volume of 100 cm<sup>3</sup>/mole are reported in Fig. 1 as plots of  $\ln K$  versus  $\sigma$ . The differences  $\delta_2 - \delta_1$  and  $\delta_2 - \delta_3$  are taken as parameters.

As an example, Table I shows two sets of numerical values of the solubility parameters corresponding to the various A and B points.

In Fig. 1, curves corresponding to values of  $\delta_2 - \delta_1$  less than 7 have not been drawn as the mutual solubility of species 2 and 1 becomes important below this value, so that from the chromatographic point of view it would not make sense to consider such systems.

It can be seen that the logarithm of the partition coefficient varies quasi-linearly with the interfacial tension when one of the two solvents 1 and 2 is changed. Much better linearity is observed, however, in the A lines than in the B lines, but even in the latter case the curvature remains slight. An important conclusion that can be drawn from Fig. 1 is that a relationship between the logarithm of the partition coefficient and the interfacial tension between the two phases must exist.

As a first approximation, the free energy of the partition process varies quasi-linearly with  $\sigma$ , provided that the mutual solubility of the two phases is small; the slope of this variation depends mainly on the solute. If this relationship is confirmed by experimental results, it would certainly be of help in choosing systems in LLC and in calculating the retention volumes in gradient elution chromatography. However, the solubility parameter theory gives an oversimplification of the actual situation. For this reason, it might be interesting to discuss a completely different theoretical approach to the problem.

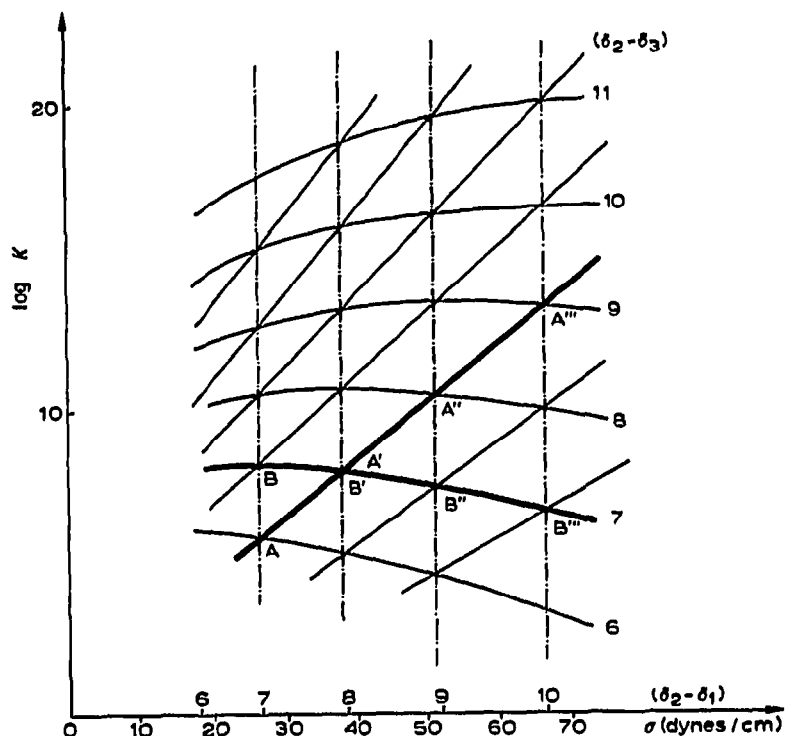


Fig. 1. Calculated logarithm of the partition coefficient of solutes as a function of the surface tension between the two liquid phases and the solubility parameter of the species. 1 and 2 = solvents; 3 = solute.

TABLE I

VALUES OF THE SOLUBILITY PARAMETERS CORRESPONDING TO VARIOUS POINTS ON FIG. 1

	A	$\delta_1$	$\delta_2$	$\delta_3$	B	$\delta_1$	$\delta_2$	$\delta_3$
First set of possible $\delta$ values	A	8	15	9	B	9	16	9
	A'	8	16	9	B'	8	16	9
	A''	8	17	9	B''	7	16	9
	A'''	8	18	9	B'''	6	16	9
Second set of possible $\delta$ values	A	5	12	6	B	6	13	6
	A'	5	13	6	B'	5	13	6
	A''	5	14	6	B''	4	13	6
	A'''	5	15	6	B'''	3	13	6

#### *Pseudothermodynamic viewpoint*

*Partition chromatography.* The Antonoff relationship states that the interfacial tension of an organic solvent against water is the difference between the surface tensions of the two phases,  $\sigma_o$  and  $\sigma_w$ , when each liquid has become saturated with the other:

$$\sigma_{o/w} = \sigma_w - \sigma_o \quad (10)$$

This very significant observation holds fairly well in most cases<sup>13,14</sup>. In the special case of water-organic solvent studied here, eqn. 10 enable the different roles played by the two phases in both the bulk and the surface to be established.

Let us imagine that the solute is eluted successively on each of these two phases by gas chromatography. In such a case, we have already demonstrated that the partition coefficient depends on the surface properties of the stationary phases through<sup>8</sup>

$$K_{R\ i(s)} = \frac{RT}{f_i^0 V_i^s \gamma_i^{L,\infty}} \cdot \exp \left[ \bar{A}_0^i (\sigma_s - \sigma_l) / RT \right] - \frac{A_0^s}{V_0^s} K_{A\ i(s)} \quad (11)$$

where, besides the usual symbols,  $f_i^0$  is the fugacity of the solute in the gas phase,  $\gamma_i^{L,\infty}$  the activity coefficient of the solute,  $i$ , in the layer that makes up the interface,  $K_A$  is the adsorption coefficient of the solute at the gas-liquid interface and  $\bar{A}_0^i$  is the partial molecular area of the solute.

When the solute is sufficiently soluble in the solvent, then its excess concentration at the interface is small and so is  $K_A$ . In such a case, the second term on the right-hand side of eqn. 11 can be neglected and we can write the conventional expression for the partition coefficient:

$$\frac{1}{\gamma_i^{\infty}(s)} \approx \frac{1}{\gamma_i^{L,\infty}} \cdot \exp \left[ \bar{A}_0^i \left( \frac{\sigma_s - \sigma_l}{RT} \right) \right] \quad (12)$$

Eqn. 11, which depends on no special assumptions, was used earlier to determine the activity coefficient of the solute at the gas-liquid interface<sup>8</sup>. Hence eqn. 12 can be assumed to be general, provided, of course, that the solubility of  $i$  in the stationary phase is so good that the  $K_A$  term can be neglected. Obviously this is not true in all instances, but eqn. 12 still explains well the results of Connors and Sun<sup>15</sup>, who found a linear relationship between the Gibbs free energy of formation of some molecular complexes with the surface tension of the liquid phase in which the reaction took place. In their study, the main solvent used was water, to which they added a large variety of additives such as sodium chloride, ethylene glycol, dioxan, methanol and acetonitrile so that the surface tension varied from 39 to 78 dynes/cm. The fact that eqn. 12 holds with such complicated solutions demonstrates its validity.

Furthermore, the good linearity of the plots obtained by Connors and Sun<sup>15</sup> confirms that the surface activity coefficients of the solute remain fairly constant over the whole range of interfacial tension, while the macroscopic bulk activity coefficients vary considerably. This point was demonstrated in our earlier work<sup>8</sup>, in which we showed that the surface activity coefficient is almost completely independent of its bulk counterpart and that it is mainly a function of the shape of the solute molecule.

As it appears that eqn. 12 is reliable, we can now express the ratio of the bulk activity coefficients in the two phases that make up the LLC system. Supposing that the partial molecular area,  $\bar{A}_0^i$ , of the solute is the same in the two interfaces, vapour-mobile phase and vapour-stationary phase, we obtain:

$$K_i \approx \frac{\gamma_i^{L,(o)}}{\gamma_i^{L,(w)}} \cdot \exp \left[ \bar{A}_0^i (\sigma_w - \sigma_o) / RT \right] \quad (13)$$

In eqn. 13, the water-rich phase is assumed to be the stationary phase. As the experimental results show that surface activity coefficients remain almost constant and independent of the bulk ones, we obtain, by combining eqns. 10 and 13:

$$\ln K_t \approx Cte + \bar{A}_0^t \frac{\sigma_{o/w}}{RT} \quad (14)$$

where the constant is the ratio of the two surface activity coefficients. Then, according to our hypothesis, the logarithm of the thermodynamic partition coefficient varies linearly with the interfacial tension between the two liquid phases, which is in agreement with the results found by using the solubility parameter theory. Combining eqns. 2 and 14, we have:

$$\ln [K_R (V_0^S / V_0^M)] = Cte + \bar{A}_0^t \frac{\sigma_{o/w}}{RT} \quad (15)$$

*Adsorption chromatography.* As most apolar organic solutes are almost insoluble in water, the only possible retention mechanism is adsorption at the organic phase-water interface. In such a case,  $K_{R(S)}$  in eqn. 11 is zero and the adsorption coefficient,  $K_A$ , of a solute at the gas-liquid interface is given by:

$$K_{A(l(w))} = \frac{RT}{f_i^0 \bar{A}_0^w \gamma_{i(w)}^{L,\infty}} \cdot \exp [\bar{A}_0^t (\sigma_w - \sigma_i)/RT] \quad (16)$$

If the solute is sufficiently soluble, there is no adsorption at the gas-mobile liquid phase interface and the gas chromatographic partition coefficient is given by

$$K_{R(l(o))} = \frac{RT}{f_i^0 V_0^o \gamma_{i(o)}^{L,\infty}} \cdot \exp [\bar{A}_0^t (\sigma_o - \sigma_i)/RT] \quad (17)$$

If it is assumed, as it should be, that each of the two phases is mutually saturated with the other, the two GLC processes can be combined in order to calculate the adsorption coefficient at the liquid-liquid interface.

Provided that the Antonoff relationship holds (eqn. 10), we can write, as a first approximation

$$K_{A(L/L)} = K_{A(G/L)} / K_{R(G/L)}$$

which, by taking eqns. 16 and 17 into account, gives

$$K_{A_t} \approx \frac{V_0^o \gamma_{i(o)}^{L,\infty}}{\bar{A}_0^w \gamma_{i(w)}^{L,\infty}} \cdot \exp \left[ \frac{\bar{A}_0^t}{RT} (\sigma_w - \sigma_o) \right] \quad (18)$$

Eqn. 18 can be written in a similar manner to eqn. 15:

$$\ln [K_A (A_0^w / V_0^o)] = Cte + \bar{A}_0^t \frac{\sigma_{o/w}}{RT} \quad (19)$$

Results from the different approaches lead to the same conclusion, which is supported by experimental results, as shown below.

## EXPERIMENTAL AND RESULTS

The interfacial tensions of some organic solvent-water systems were measured at 25° with the help of a Leconte Du Nouy tensiometer. The results are reported in Table II. We then measured the retention volumes with a home-built liquid chromatograph equipped with a differential refractometer detector. Depending on the system used, Sovirel porous layer glass beads, 36–75  $\mu$ , were coated either with the organic solvent or with water. In the former case, water was used as the mobile phase, while the organic solvent was used as mobile phase in the latter case. The solutes studied were cyclooctane, *n*-propylaldehyde, acetone, di-*n*-propyl ether, butyl and ethyl alcohols and butyric and acetic acids.

TABLE II  
INTERFACIAL TENSION BETWEEN WATER AND VARIOUS SOLVENTS

Solvent	$\sigma_{olw}$ (dynes/cm)
Amyl acetate	14.6
Olive oil	18.2
Nitrobenzene	25.6
Nitrobenzene-toluene (1:1)	31
Toluene	36
Cyclooctane	41
Heptane-toluene (1:1)	42.2
Heptane	50.5

In order to avoid the determination of the surface area of the interface,  $A_I$ , we kept this quantity constant by using a constant loading of the support.

As neither  $K_R$  nor  $K_A$  was calculated, the results are reported as  $V'_0$ , the retention volume of a solute per gram of water used as the stationary phase, loaded at 10% on Sovirel porous glass beads. The results are illustrated in Figs. 2–5. It can be seen that a linear relationship is always found when the interfacial tension between the two phases is greater than about 25 dynes/cm. Below this value, we found either a curvature of the plot (Figs. 2 and 3) or even a break in the curve, as is the case for the acids in Fig. 5. This last point has already been mentioned by Vignes<sup>6</sup> and we do not yet understand the reason for such a rapid change. However, in the near future we intend to publish results obtained with systems of very low interfacial tension (less than 10 dynes/cm) and to show that eqn. 14 cannot hold in such cases. Nevertheless, it can be concluded from the present experimental results that eqn. 14 is valid for a large range of interfacial tensions, provided that this tension is sufficiently high.

As an additional proof, it is worth noting that the slope of the curves is always positive, as it should be from eqn. 14. Furthermore, the slope of the linear part of curve 2 in Fig. 3 gives  $A'_0 = 2.26 \cdot 10^9$ . Using the crude approximation that  $A'_0 = (V'_0)^{2/3} N^{1/3}$ , we obtain  $V'_0 \approx 140$  cm<sup>3</sup>/mole. As the true molar volume of propyl aldehyde is 90 cm<sup>3</sup>/mole, it is clear that our model is physically correct.

The fact that the slope of the straight lines obtained for the alcohols in Fig. 4 is much less than it should be can be explained by the very strong orientation of the



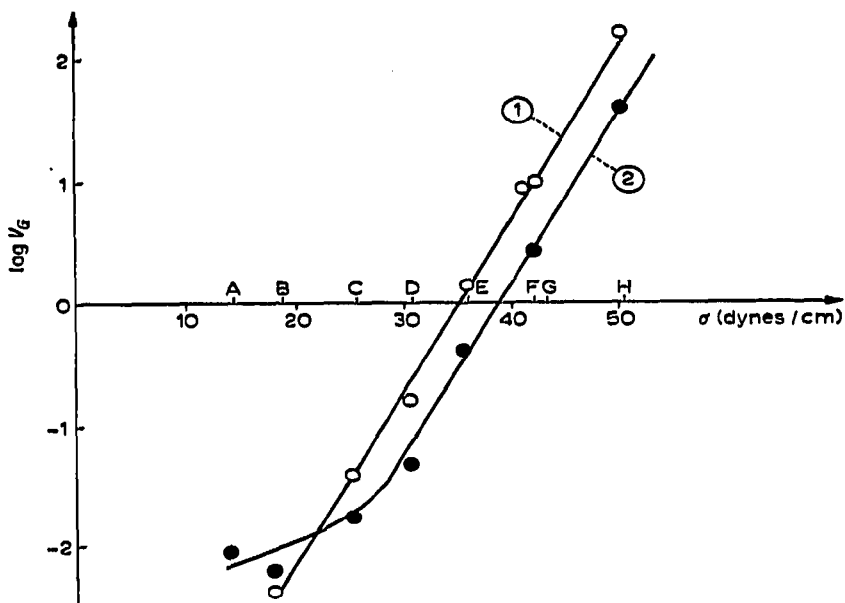


Fig. 2. Variation of the logarithm of the retention volume as a function of the interfacial tension between the two liquid phases. Systems: A = amyl acetate-water; B = olive oil-water; C = nitrobenzene-water; D = 1:1 nitrobenzene + toluene-water; E = toluene-water; F = cyclooctane-water; G = 1:1 heptane + toluene-water; H = heptane-water. Solutes: 1 = amyl acetate; 2 = *n*-butyl acetate.

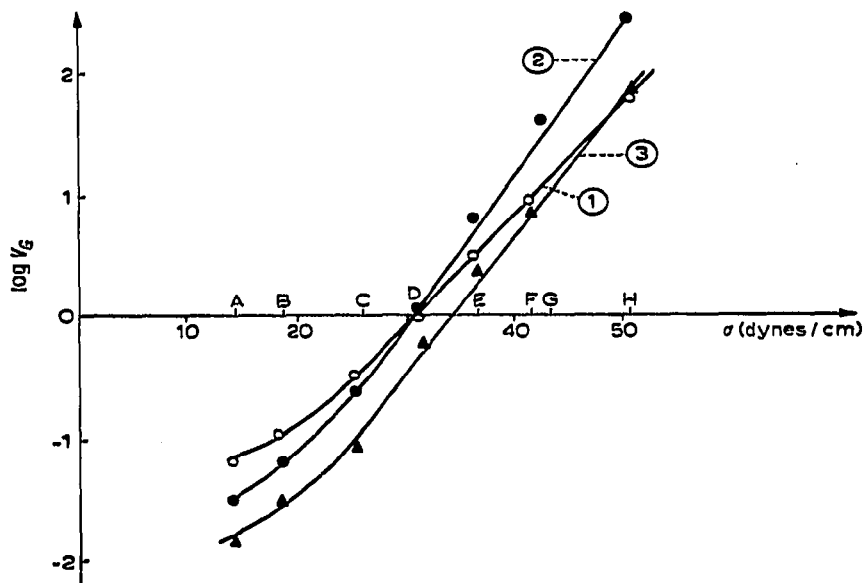


Fig. 3. As Fig. 2, except for solutes: 1 = cyclooctane; 2 = *n*-propyl aldehyde; 3 = acetone.

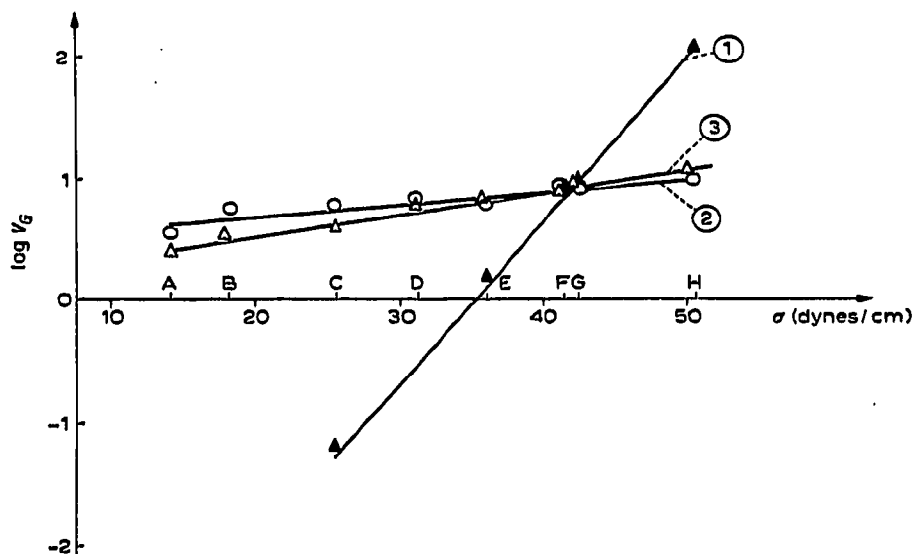


Fig. 4. As Fig. 2, except for solutes: 1 = di-*n*-propyl ether; 2 = butyl alcohol; 3 = ethyl alcohol.

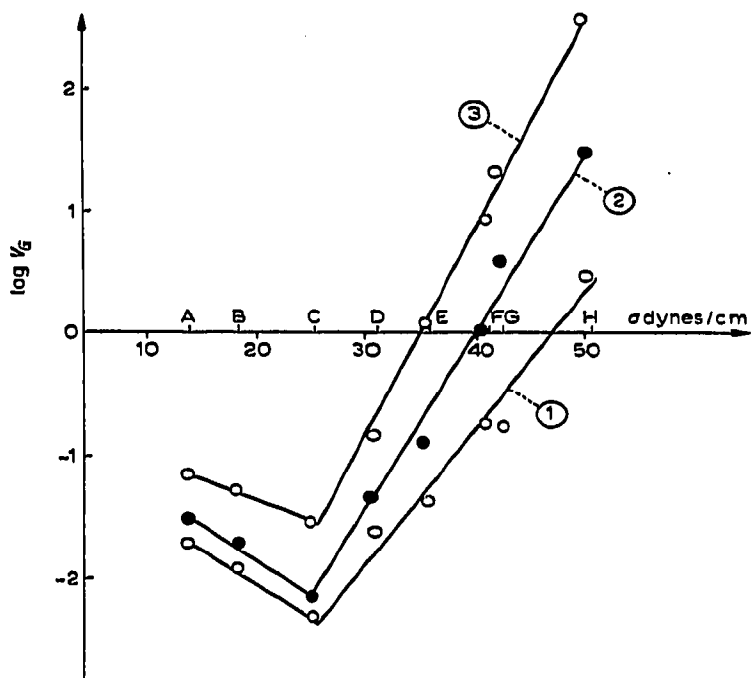


Fig. 5. As Fig. 2, except for solutes: 1 = butyric acid; 2 = propionic acid; 3 = acetic acid.

alcohol molecules at the organic solvent-water interface, and in this case  $K_A$  in eqn. 11 cannot be neglected. However, it is interesting to observe that the partition coefficient still varies exponentially with the interfacial tension.

The application of the relationship obtained is discussed below.

## DISCUSSION

We have shown above that the chromatographic partition coefficient obeys eqn. 15 for a large range of interfacial tensions. Such a relationship is important and can be of help to chromatographers in at least three ways:

(1) *Prediction of the retention volumes.* It is obvious from the plots in Figs. 2-5 that the linearity of the curves permits the prediction of the retention volumes for organic solvent-water systems whose interfacial tensions are known.

(2) *Choice of the system.* The plots in Figs. 2-5 enable the best system for performing a given analysis to be chosen. As an example, Fig. 3 shows that a system with an interfacial tension of 40 dynes/cm is suitable for separating cyclooctane, *n*-propylaldehyde and acetone, whereas systems with interfacial tensions of 30 or 50 dynes/cm could not be used.

(3) *Estimation of the retention volume in gradient concentration chromatography.* One of the advantages, perhaps the main one, of eqn. 15 is that it seems also to be valid when two solvents are mixed, as for mixtures of heptane with toluene and of nitrobenzene with toluene. Of course, it cannot yet be predicted whether such behaviour can be expected in all cases; however, it is easy to make a check by measuring partition coefficients and surface tensions for the pure solvents and for a 1:1 mixture of the two required solvents. Whenever the plot obtained is linear, the retention time of the solute for any gradient programme can be calculated.

If it is assumed that the molar volume of the mobile phase does not vary much with its composition, then the chromatographic partition coefficient varies as

$$K_R = K_R^0 \exp(Z \sigma_{o/w}) \quad (16)$$

The retention time is given by integration of the migration velocity of the solute. This velocity at a given time is given by

$$\frac{dz}{dt} = F \frac{L}{V} \quad (17)$$

where  $F$  is the flow-rate,  $L$  the length of the column and  $V$  the retention volume at the corresponding time. Integration between the column inlet and outlet gives

$$\frac{1}{L} \int_0^L dz = 1 = \int_{t_0}^t \frac{1}{V} dt \quad (18)$$

If the gradient is programmed in such a way that the interfacial tension decreases linearly with increasing time:

$$\sigma_{o/w} = \sigma_{o/w}^0 - bt \quad (19)$$

$dt$  is obtained by differentiation of eqn. 19 and, by combination with eqn. 1, 16 and

18, we have

$$1 = -\frac{F}{b} \int_{\sigma_{o/w}^0}^{\sigma_{o/w}^R} \frac{d\sigma_{o/w}}{V_m + K_R^0 V_l \exp(Z\sigma_{o/w})} \quad (20)$$

where  $V_m$  is the dead volume of the column and  $\sigma_{o/w}$  the interfacial tension of the system at the retention time  $t_R$ .

The integral of eqn. 20 is

$$\left[ \frac{\sigma_{o/w}}{V_m} - \frac{1}{V_m Z} \left( \ln V_m + K_R^0 V_l \exp(Z\sigma_{o/w}) \right) \right]_{\sigma_{o/w}^0}^{\sigma_{o/w}^R} \quad (21)$$

Taking into account that  $t_R = (\sigma_{o/w}^0 - \sigma_{o/w}^R)/b$ , then upon substitution  $\sigma$  within eqn. 21 and re-arrangement we can calculate the retention time:

$$t_R = \frac{1}{bZ} \ln \left( 1 + \frac{K_R^0 V_l}{V_m} \exp(Z\sigma_{o/w}^0) \left[ \exp \left( ZV_m \frac{b}{F} \right) - 1 \right] \right) \quad (22)$$

Eqn. 22 enables the retention time to be calculated in the case of a linear variation of the interfacial tension with the time. It is given as an example, and any other programme can be treated in a similar manner by changing eqn. 19.

In any particular case, however, we have to know the variation of the interfacial tension of the system with the composition of the organic phase over the whole range of concentrations used. Unfortunately, no general law has yet been established that would permit such a curve to be computed from only the interfacial tensions of the two extreme systems, solvent 1–water and solvent 2–water. This is certainly a major inconvenience, but the measurements can be made simply and quickly by using fairly simple equipment. Furthermore, this determination, once made, is applicable to any solute for which only a few values of the partition coefficient have to be obtained in order to determine the slope of the line  $\ln K$  versus  $\sigma$ . It will certainly be useful for studying systematically the interfacial tensions of ternary systems in the near future.

## CONCLUSION

This work shows that the interfacial tension between two liquid phases is a decisive parameter for the prediction of the selectivity of systems in liquid–liquid chromatography. The good linearity of the plots of the logarithm of the partition coefficient versus the interfacial tension between the mobile and the stationary phases permits the accurate prediction of the retention volumes for several varieties of systems and permits a judicious choice of the composition of the mobile phase of the gradient programme in order to perform a given analysis.

Although our determinations have dealt only with organic phase–water systems, the coherent theory that we have established leads us to expect that other types

of systems should behave in the same way, provided that no strong adsorption occurs at the interface and that the Antonoff rule holds.

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