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THE CONTRIBUTION OF SOLUTION AND ADSORPTION PHENOMENA IN GAS–LIQUID PARTITION CHROMATOGRAPHY SYSTEMS IN WHICH INFINITE DILUTION OF SOLUTE MAY BE ASSUMED

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SUMMARY

The retention volume is assumed to consist of three parts: bulk liquid solution, solid surface adsorption and liquid–gas interface adsorption. A method is presented for the quantitative evaluation of these parts by chromatography alone, when all three retention mechanisms occur.

INTRODUCTION

Recently a series of papers[1–3] have been published on retention factors in gas–liquid partition chromatography (GLPC). The most interesting is the first paper, by CONDER *et al.*[1], which includes not only an exhaustive discussion of earlier work done in this field but also many new ideas. The total retention volume is considered to consist of three parts, due to the existence of three retention mechanisms: bulk liquid solution, support surface adsorption and adsorption by the liquid surface. Next, the dependence of these retention mechanisms on solvent volume, mode of wetting of the support by the liquid and on the sample size of the solute is considered for a variety of practical situations. The theoretical and experimental problems are comprehensively discussed and related to the evaluation of the contributions of all these retention mechanisms to the total retention volume.

However, a certain problem of a theoretical and practical nature remains unresolved. "For chromatographic systems in which all three mechanisms occur, only the bulk liquid partition coefficient can be determined unequivocally by chromatography alone" — quoting CONDER *et al.*[1].

We propose in this paper a method for determining all three partition coefficients unequivocally by chromatography alone, for the case of infinite dilutions of solute and for the region of higher coverages of supports by liquids. Moreover, the method allows for the quantitative determination of contributions from all three retention mechanisms to the total retention volume by the use of chromatographic data alone.

THEORY

The starting point of our calculations is retention theory in the form presented by CONDER *et al.*[1]. This theory will be modified to give a more realistic treatment of adsorption phenomena in GLPC systems.

Following CONDER and coworkers we distinguish three sources of solute retention in GLPC. These are: bulk liquid solution, solid–liquid interface adsorption and adsorption at the gas–liquid interface. Both kinds of adsorption mentioned above are considered as fully two-dimensional. Accordingly, the number, n, of moles of solute held stationary in the column in equilibrium with a concentration c in the free gas phase is:

$$n = q_l V_l + q_i A_i + q_s A_s \tag{1}$$

where: V_l is the volume of the bulk liquid; A_i and A_s are the surface areas of the liquid and of the support, respectively; q_l, q_i and q_s are the solute concentrations in the bulk liquid, gas-solid interface and support–liquid interface, respectively.

Since the adsorption phenomena are considered to be two-dimensional, the two last concentrations, q_i and q_s, are expressed as the number of moles of solute per unit surface area.

The total retention volume V_N as observed experimentally is given by:

$$V_N = (1 - jy_0) \frac{dn}{dc} \tag{2}$$

where j is the James–Martin compressibility factor, and y_0 is the mole fraction of solute corresponding to the concentration c at the column outlet.

As was mentioned above, only the case of infinite dilutions of solutes will be considered in this paper. In this case CONDER's expression for the retention volume reduces to the following simple equation:

$$V_N = K_l V_l + K_i A_i + K_s A_s \tag{3}$$

where:

$$K_m = \frac{q_m}{c} \text{ and } m = l, i \text{ or } s.$$

As did CONDER, we neglect the effects connected with the dynamic character of chromatographic processes.

CONDER's assumption of the two-dimensional character of the adsorption phenomena is an approximation which should not be accepted *a priori*, but should be verified by some more general calculations. From the potential theory of adsorption[4], at the present time the most general one, it follows that both the gas–liquid and the support surface adsorption take place in three-dimensional spaces which are parts of the total volume V_Σ of the chromatographic column.

We divide the volume V_Σ into the following parts: (1) the volume of the solid support, V_a; (2) the volume of the space where the adsorption by the support surface takes place, V_s; (3) the volume, V_l, where the bulk liquid partition takes place;

this volume is considered to be simply equal to the volume of the liquid used in covering the support; (4) the volume, V_t, where the adsorption by the liquid surface takes place; (5) the free gas phase volume, V_f.

Thus:

$$V_\Sigma = V_a + V_s + V_l + V_i + V_f \tag{4}$$

As is customary we shall call $(V_s + V_l + V_t + V_f)$ the total volume, V_t, and $(V_s + V_l + V_t)$ the volume of the surface phase.

The basis of chromatographic processes is the difference between the potential energies of solute molecules in the surface and in the free gas phase. In the case of infinite dilutions of solutes, the interactions between solute molecules may be neglected and the potential energy of solute molecules derives only from the support–solute and liquid–solute interactions. These two interactions differ of course from their isolated counterparts since in the present system they are not independent of each other and perturbations occur. However, while the support–solute interactions are rather strongly perturbed by the presence of liquid, the liquid–solute interactions should be only slightly affected by the presence of solid (in the bulk phase, as well as on the liquid surface). For example, in URONE's opinion[5] only the layer of the liquid molecules lying nearest to the solid surface is affected by the presence of solid (the so-called modified layer).

It is not necessary for our theory to know to what degree the solid–solute and the liquid–solute interactions themselves interact. The degree of perturbation will derive naturally from our calculations.

We assume only that the solute molecules have some potential energy, E_m, in the volumes V_m ($m = a, s, l, i$ or f). Next we state that $E_a = +\infty$ and $E_f = 0$. Thus, the total potential energy $E(\boldsymbol{r})$ of a solute molecule whose centre is at the point $\boldsymbol{r}$ is assumed to be:

$$E(\boldsymbol{r}) = \begin{cases} +\infty & \text{for } \boldsymbol{r} \in V_a \\ E_s & \text{for } \boldsymbol{r} \in V_s \\ E_l & \text{for } \boldsymbol{r} \in V_l \\ E_i & \text{for } \boldsymbol{r} \in V_i \\ 0 & \text{for } \boldsymbol{r} \in V_f \end{cases} \tag{5}$$

From statistical mechanics it follows that E_m is the so-called "potential of average force" acting on one considered molecule from all support and liquid molecules. Moreover, it can be seen that the above square-well potential is fully valid only for simple solute molecules having spherical symmetry and exhibiting non-specific interactions with support and liquid molecules. However, our theoretical treatment may be easily extended to the case of solute molecules having a more complicated structure. This can be done by introducing the concept of effective interaction energy, $E(\boldsymbol{r})$, which is simply the appropriate energy $E(\boldsymbol{r})$ averaged over all molecular coordinates, except for the centre of mass.

As is customary we shall refer to the potentials E_l, E_s and E_t as the energy of solution, the energy of support surface adsorption and the energy of adsorption by the liquid surface, respectively. The relationships between the potentials E_m and thermodynamic functions will be discussed in detail in the APPENDIX.

Since the interactions between the solute molecules are neglected, there exists a simple relationship between the energies E_m and the coefficients K_m:

$$K_m = \exp\left[\frac{-E_m}{kT}\right] \tag{6}$$

where k is the Boltzmann constant and T is the absolute temperature.

Of course in our model of the adsorption phenomena all concentrations $q_m = cK_m$ are expressed as the number of solute moles per unit volume. Consequently:

$$V_N = \sum_m V_m \exp\left[\frac{-E_m}{kT}\right] \tag{7}$$

Now, suppose we wish to know the value $X(1/T)$ defined by:

$$X\left(\frac{1}{T}\right) = V_N - K_l V_l \tag{8}$$

for a number of temperatures (at least four). It can be easily obtained from the plot of V_N/V_l against $1/V_l$. With this notation we rewrite eqn. 7 in the form:

$$\ln V_s - \frac{E_s}{kT} = \ln\left\{X\left(\frac{1}{T}\right) - V_l \exp\left[\frac{-E_l}{kT}\right]\right\} \tag{9}$$

From the last equation it follows that its right-hand side plotted against $1/T$ should yield a straight line having a slope $-E_s/k$ and intercept $\ln V_s$. However, to plot this line one must know *a priori* the volume V_l and the energy E_l. We propose the following procedure for resolving this problem.

Let us choose the values V_l and E_l so that they should yield a straight line when plotting the right-hand side of eqn. 9 against $1/T$, with values X $(1/T)$ found experimentally. In this way we also obtain the values V_l and E_l as V_s and E_s.

However, there exist difficulties in interpreting the results of the procedure described. They are connected with the symmetry of eqn. 9, which may also be written in the form:

$$\ln V_l - \frac{E_l}{kT} = \ln\left\{X\left(\frac{1}{T}\right) - V_s \exp\left[\frac{-E_s}{kT}\right]\right\} \tag{10}$$

By using this procedure one obtains two pairs of values of V and E, but it is not possible to ascribe these pairs to corresponding kinds of adsorption phenomena.

Thus, some additional tests must be carried out to correlate each pair to either the adsorption by the support or by the liquid surface. These tests may be either of an experimental or theoretical nature. The method of identification depends on the GLPC system under consideration, and above all on the inventiveness of the investigator.

Of course computers must be used in the calculation procedure described above, but there seems to be no difficulty in using this procedure nowadays.

EXPERIMENTAL

For the support Polsorb C was used, having a specific surface area of 3.17 m^2/g and particle diameter 0.1–0.3 mm. This support was covered with dinonyl phthalate, using the dynamic method of PARCHER and URONE[6]. In this way three GLPC systems were obtained, containing 1 %, 2 % and 5 % w/w of liquid, respectively.

Two substances, cyclohexane and carbon tetrachloride, were examined. Three different sample sizes, 0.05, 0.1 and 0.3 μl, were used. It was found that for these sample sizes the retention volume remained practically constant. We are of the opinion that we have probably reached concentrations very near to infinite dilution.

Hydrogen was used as the carrier gas and cleaned by means of molecular sieve type 5A. The flow-rate was about 75 ml/min.

The reagents used were dinonyl phthalate, British Drug Houses, Great Britain, and cyclohexane and carbon tetrachloride, POCh Gliwice, Poland.

RESULTS AND DISCUSSION

In Table I the results of our measurements and calculations are presented. The values of $X(1/T)$ were obtained by using the procedure recommended by CONDER[3], *i.e.* by subtracting from V_N the value $K_l V_l$, with K_l found from a plot of V_N/V_l against $1/V_l$.

The numerical calculations were performed by means of the computation procedure of FLETCHER AND REEVES[7].

ABLE I

ARTITION AND ABSORPTION DATA FOR CYCLOHEXANE AND CARBON TETRACHLORIDE

	Temperature (°C)									
	Cyclohexane					*Carbon tetrachloride*				
	50	*65*	*80*	*100*	*120*	*50*	*65*	*80*	*100*	*120*
$(1/T)$	2.05	1.16	0.75	0.44	0.24	2.32	1.36	0.84	0.46	0.27
$_l$ (cal/mole)	2969					3132				
$_l$ (cm^3)	$5 \cdot 10^{-2}$					$5 \cdot 10^{-2}$				
ontribution to bulk liquid partition (%)	87.4	87.9	88.5	89.3	89.8	16.7	19.7	23.1	26.8	30.9
$_t$ (cal/mole)	7191					8887				
$_t$ (cm^3)	$1.52 \cdot 10^{-5}$					$5.59 \cdot 10^{-5}$				
ontribution to liquid surface absorption (%)	11.9	11.2	10.3	9.5	8.7	82.5	79.6	76.4	72.5	68.6
$_s$ (cal/mole)	3807					3888				
$_s$ (cm^3)	$1.80 \cdot 10^{-4}$					$1.56 \cdot 10^{-5}$				
ontribution to support surface absorption (%)	0.7	0.9	1.2	1.2	1.5	0.8	0.7	0.5	0.7	0.5

According to the theoretical assumptions expressed above, two pairs of values of V and K for each GLPC system were obtained, presented in Table I. The identification of these pairs was made as follows.

For this purpose we evaluated the pairs V_s, K_s in the appropriate gas–solid chromatography (GSC) systems, using pure Polsorb C. The energies E_s calculated from the coefficients K_s were 3578 and 4587 cal/mole for cyclohexane and carbon tetrachloride, respectively. We are of the opinion that in spite of the probable large mutual perturbations in the support–solute and in the liquid–solute interactions, the energy E_s in a GSC system should be closer than E_t to the value of E_s in the appropriate GLPC system.

In Table I data are presented for the pairs V and E and also for the contributions of the appropriate retention mechanisms to the total retention volume. It can be seen from Table I that bulk liquid solution is the predominant retention mechanism in the case of cyclohexane while for carbon tetrachloride the predominant retention mechanism is the liquid surface adsorption.

It is of further interest to consider the case of the support wetted fully and uniformly by the stationary phase. In CONDER's[1] opinion this occurs at higher liquid loadings, at solvent: support ratios higher than 5 % w/w.

The values of V and E presented in Table I concern a liquid loading of about 5 % w/w. Thus one should expect at this solvent:support ratio good wetting of supports by liquids.

Suppose now that the support–liquid interface area is equal to that of the support–gas interface, and that the liquid is uniformly distributed on the support. With these assumptions we are able to calculate the gas–support interaction depth in the presence of liquid. It is simply equal to V_s/S, where S is the gas–support interface area (measured in the appropriate GSC system).

It has been found by the Brunnauer–Emmet–Teller (BET) method using benzene as adsorbate that the gas–support interface area of our support (Polsorb C) is equal to 3.17 m²/g. This gives for the gas–solid interaction depths (in the presence of liquid) the values $0.48 \cdot 10^{-9}$ and $1.77 \cdot 10^{-9}$ cm for cyclohexane and carbon tetrachloride, respectively.

Assuming that the gas–liquid interface area is equal to the gas–support interface area, we get for the gas–liquid interaction depth the values $0.57 \cdot 10^{-8}$ and $0.45 \cdot 10^{-9}$ cm for cyclohexane and carbon tetrachloride, respectively.

Thus, if the above assumptions were fulfilled by our GLPC systems, CONDER's[1] assumption of the two-dimensional character of both adsorption phenomena would be a good approximation in this case.

Consider now the problem, which is of special importance from both the theoretical and practical points of view, of how to predict the total retention volume over a wide range of temperatures and stationary phase loadings.

The problem can be fully resolved mathematically by using the relationships developed above and also some experimental facts reported in CONDER's papers. Our theory concerns the case of higher liquid loadings where, following data reported by CONDER[1], both V_s and V_t remain practically unchanged when the solvent: support ratio increases. Thus, the retention volume V_N is a simple function of the variables V_l and T. This function includes E_l, E_s, E_t, V_s and V_t as parameters.

APPENDIX

Consider the thermodynamic functions of a solute in the zones V_m. The partition function f_m for a single molecule in the zone V_m is:

$$f_m = \left(\frac{2\pi\omega kT}{h^2}\right)^{\frac{3}{2}} V_m \left\{\exp\left[\frac{-E_m}{kT}\right]\right\} f_{\text{in}} \tag{11}$$

where ω is the mass of solute molecule, and f_{in} is the molecular partition function connected with the internal degrees of freedom.

Since the potential model of adsorption is assumed, the molecules in the zones V_m form systems of non-localized molecules. Thus, the system partitition function $f_{M,m}$ for M molecules in the zone V_m is:

$$f_{M,m} = \frac{(f_m)^M}{M!} \tag{12}$$

The Helmholtz function A_m is:

$$A_m = -kT_s \ln f_{M,m} \tag{13}$$

The other relationships may be obtained from the obvious fact that the chemical potentials μ_m of the solute must be equal. Thus:

$$\mu_l = \mu_s = \mu_i = \mu_f \tag{14}$$

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