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## ADSORPTION FROM LIQUID MIXTURES AND LIQUID CHROMATOGRAPHY\*

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### SUMMARY

It is shown that retention volumes can be calculated in terms of the total material content in the chromatographic column as transported by the eluent, termed the "column capacity". With the aid of this retention equation, of general validity, the necessary link is established between Gibbs' description of adsorption at a liquid-solid interface and the theory of retention in liquid-solid chromatography. Relationships are given for the correct interpretation of retention volumes and for the chromatographic determination of adsorption isotherms of the components in a binary liquid mixture.

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### INTRODUCTION

In the mathematical treatment of multi-component chromatography by De Vault<sup>1</sup>, retention volumes are found to be the eigenvalues of a matrix, the elements of which are the partial derivatives of the partition isotherms with respect to the concentration in the mobile phase. Baylé and Klinkenberg<sup>2</sup> and Mangelsdorf<sup>3</sup> pointed out very clearly that conclusions drawn from this model can be considered valid only if it can be shown that the matrix has real, positive eigenvalues. At present there is no thermodynamic proof of general validity; a demonstration was given only for some special cases by Mangelsdorf<sup>3</sup> and Helfferich and Klein<sup>4</sup>. Perhaps it is because of this basic difficulty that the results of this treatment were never applied to a quantitative evaluation of experiments. Further, the link was never obvious between the theory of adsorption from liquid mixtures and that of liquid-solid chromatography. This question has already been treated by De Vault<sup>1</sup> and later by Schay<sup>5</sup>, but the application of their theoretical results to experiment is not without difficulties, as it is shown by several more recent papers<sup>6-15</sup> on the determination of hold-up volumes and composite adsorption isotherms.

In this paper we propose an interpretation of experimental data in liquid chromatography that is coherent with the theory of adsorption. Restrictions had to be introduced for the general validity of the conclusions; they are in relation to the lack

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\* Based on the doctoral thesis of F. Riedo.

of a solution of the fundamental eigenvalue problem. Also, an experimental method for the determination of composite isotherms in binary liquid mixtures is discussed.

#### RETENTION IN THE CHROMATOGRAPHIC COLUMN UNDER ANALYTICAL CONDITIONS

In the *classical model of the chromatographic process* a solute is distributed between two homogeneous phases of well defined boundary and extent, one of which is mobile and the other stationary. The identification of such phases in different types of chromatography is not always obvious. For example, in liquid–solid chromatography with a mixture as the eluent there exists in the liquid, normal to the eluent–solid interface, a concentration gradient. Experimental evidence shows that far enough from the interface there is liquid of homogeneous composition but no definite boundary can be established between the homogeneous portion inside the liquid and the certainly non-homogeneous surface phase. In the dynamic chromatographic system there arises a further boundary problem, namely that between the mobile part of the eluent (supposedly of homogeneous composition) and the stationary layer near the surface. A final problem is the identification of an eluent in the sense of a “carrier of solutes”. Actually, in this respect there is no difference between components of the eluent and those of the sample; in the column every compound is once part of the carrier and then part of the stationary layer. Liquid–solid chromatography is a typical example of “multi-component chromatography with interference” as defined by Helfferich and Klein<sup>4</sup>. It can be concluded that in these instances the classical model is not adequate to describe the chromatographic process because the identification of a homogeneous stationary phase is not possible. Obviously, concepts intimately related to this model such as partition coefficient and hold-up volume also have no evident interpretation.

In the following, a *new approach* is proposed and it will be shown that it is possible to describe the chromatographic process with the aid of a function called the “column capacity” and by only supposing that there is a homogeneous mobile phase (referred to by the subscript  $\mu$ ) which has a material content greater than zero. It will be shown that in the general case the exact value of this material content (and of the corresponding volume) can be left unspecified. If useful or necessary it can be determined from case to case on the basis of a model (e.g., gas–liquid chromatography) or a convention (e.g., liquid–solid chromatography).

For the *definition of the column capacity* let us consider an infinite amount of a fluid  $m$ -component mixture (liquid or gas) of the composition  $\bar{x}_\beta$ , where the subscript  $\beta$  refers to this bulk. The composition is designated by an  $m-1$ -dimensional vector with the individual molar fractions,  $x_{\beta,i}$ , as components:

$$\bar{x}_\beta = (x_{\beta,1}, \dots, x_{\beta,i}, \dots, x_{\beta,m-1}) \quad (1)$$

(the composition can also be given in terms of mass fractions,  $\bar{f}_\beta$ , or volume fractions,  $\bar{v}_\beta$ ). Let us also imagine a rigid tube filled with a well defined amount of a non-volatile powder absolutely insoluble in the aforementioned fluid. The nature of the powder is left unspecified. The tube closed at the ends by membranes permeable to the fluid is now considered as the system to be characterized. It is placed into the fluid mixture at temperature  $T$  and pressure  $P$ . After equilibrium is established the fluid is completely

emptied from the tube and the mass, composition and nature of the fluid yield are determined. This result expressed in terms of number of moles is deemed the "molar capacity vector of the tube",  $\vec{n}_k$ . One of the components of this vector is the "molar component capacity", *i.e.*, the total amount of a compound contained in the tube. At constant temperature and pressure these  $m$  functions depend on the composition of the fluid mixture:

$$n_{k,i} = n_{k,i}(\vec{x}_\beta) \quad (2)$$

They are equilibrium properties of the tube and as such characterize its equilibrium state. Equivalently, the total molar capacity

$$n_{k,tot} = \sum_{i=1}^m n_{k,i} \quad (3)$$

together with the composition vector of the yield,  $\vec{x}_k$ , also define the equilibrium state of the tube. In non-trivial cases  $\vec{x}_k \neq \vec{x}_\beta$ .

It will be now shown that if this tube is used as a *chromatographic column* where any compound admitted in the chromatographic process (including the sample, eluent, etc.) was included in the set of  $m$  substances then the  $m$  functions  $n_{k,i}(\vec{x}_\beta)$  determine unequivocally the retention properties of the column under the following conditions:

(a) The process must be considered to proceed through states of equilibrium (instantaneous equilibrium at any point inside the column) because the value of the column capacity refers to equilibrium. Any other knowledge about the retention, *e.g.*, retention mechanism, is not necessary.

(b) The hypothesis of the existence of a homogeneous mobile phase of non-zero and positive material content must be admissible and plausible. It will be identified as part of the fluid mixture from the foregoing experiment; consequently, the column capacity will refer to the composition of this phase. However, the extent of the volume of the mobile phase need not be specified.

So far, the model as presented has been very general. For proper mathematical treatment it is necessary to specify further the chromatographic system. The *idealized chromatographic column* which will be referred to (see Fig. 1) has a uniform cross-section at any distance,  $z$ , from the inlet ( $z = 0$ ) to the outlet ( $z = L$ ). It is filled with a quasi-continuum of a porous column material with pores uniformly and microscopically distributed. It is not necessary at this stage to specify the material and composition of the column filling (solid, solid support coated with a liquid, solid with chemically modified surface, etc.). A fluid  $m$ -component mixture is made to flow through the column at constant temperature,  $T_c$ . It experiences no flow resistance, and consequently the pressure in the column is uniform,  $\bar{P}_c$  (mean column pressure). In this dynamic situation the composition of the mobile phase becomes a function of distance along the column and time,  $\vec{x}_\mu(z,t)$ . The interface separating the eluent and the column material has a total area  $S$ . The mobile phase advances through the column with a piston flow profile. As previously noted, it has a positive volume but the exact value will be left unspecified. A detector is placed at the column outlet to measure the composition  $[\vec{x}_\mu(z=L,t)]$  of the mobile phase. In order to simplify the

description of the dynamic behaviour of the system, the usual assumptions are introduced: instantaneous equilibrium in each cross-section and no axial diffusion. The only novel hypothesis to be made is that within any cross-section that part of the fluid mixture which has a different composition from that of the mobile phase  $x_\mu(z,t)$  remains stationary. For such a column the column capacity is an intensive function if referred to unit column length,  $\bar{n}_k/L$ .

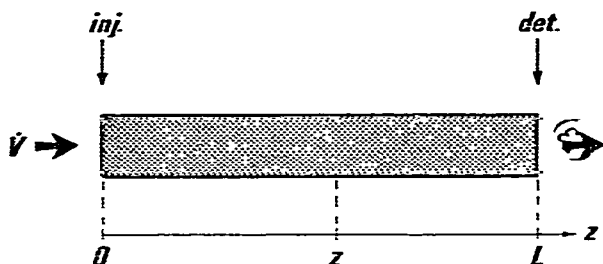


Fig. 1. Scheme of the chromatographic column filled with a quasi-continuum of a porous powder.

We now address the usual problem encountered in elution chromatography, *i.e.* that of the *retention volume*,  $V_{R,i}$ , of a concentration signal introduced at the beginning of the column but in terms of the vector function

$$\bar{n}_k = \bar{n}_k(\bar{x}_\mu) \quad (4)$$

Within any cross-section the material content can only change through material transport by the eluent. Therefore for compound  $i$ , the material balance in the section from the column inlet to distance  $z$  is given by the equation

$$\begin{aligned} \int_0^z \{[n_{k,i}(\bar{x}_\mu(z,t))]/L\} dz = & \int_0^z \{[n_{k,i}(\bar{x}_\mu(z,0))]/L\} dz + \\ \text{Material content in the} & \text{Material content in the} \\ \text{section } (0-z) \text{ at time } t & \text{section at time } t = 0 \\ + \int_0^t [\dot{V}(0,t)x_{\mu,i}(0,t)/v_\mu(\bar{x}_\mu(0,t))] dt - & \int_0^t [\dot{V}(z,t)x_{\mu,i}(z,t)/v_\mu(\bar{x}_\mu(z,t))] dt \\ \text{Amount of compound } i & \text{Amount of compound } i \text{ which} \\ \text{which entered at } z = 0 & \text{left the section at } z \end{aligned} \quad (5)$$

$i = a, \dots, m$ , where the term  $\dot{V}(z,t)$  represents the flow-rate considered to be a function of  $z$  and  $t$  and  $v_\mu$  is the mean molar volume of the mobile phase. Partial differentiation of eqn. 5 first with reference to time and then to length gives the differential equation of the material balance as follows:

$$(1/L) \frac{\partial}{\partial t} [n_{k,i}(\bar{x}_\mu(z,t))] = - \frac{\partial}{\partial z} [\dot{V}(z,t)x_{\mu,i}(z,t)/v_\mu(\bar{x}_\mu(z,t))] \quad (6)$$

With suitable initial and boundary conditions, this set of  $m$  partial differential equa-

tions determines the  $m$  functions in question:  $m - 1$  composition functions,  $x_{\mu,i}(z,t)$ , for the components  $a, \dots, i, \dots, (m - 1)$  and the  $m$ th function, the flow-rate,  $V(z,t)$ . It is shown in the Appendix that, by an appropriate change of variables, the system can be reduced to a set of  $m - 1$  equations for the components of the unknown composition vector  $\bar{x}_{\mu}(z,t)$ .

Seeking a specific solution for *analytical chromatography under isothermal and isocratic* conditions, appropriate initial conditions are now given as follows. Prior to chromatography the column is equilibrated with the eluent which is an  $N$ -component mixture of the composition  $\bar{x}_{\mu}^0$  with components designated by capital letters A, ..., J, ..., N. The superscript zero refers to the time  $t = 0$  when the column is ready for injection and eluent of identical composition will enter at the inlet ( $z = 0$ ) and leave at the outlet ( $z = L$ ), suggesting that this is also the composition of the mobile phase throughout the column:

$$\bar{x}_{\mu}(z,t=0) = \text{constant} = \bar{x}_{\mu}^0 \tag{7}$$

At the time  $t = 0$  the composition of the incoming mixture is modified by injection of an infinitesimal sample. This will introduce a composition change in a small section of the column. As the signal is infinitesimal, only the case of one solute will be treated, as at infinite dilution the solutes do not interact and their retention volumes are independent of one another (see also Appendix). The vector  $\bar{x}_{\mu} = \bar{x}_{\mu}(z,t)$  is the composition vector of the eluent also containing a solute,  $\bar{x}_{\mu,su}$ . For reasons of uniformity and (as will be seen later) of simplicity, the molar fraction of one of the components of the eluent will always be considered as the dependent variable  $\bar{x}_{\mu} = (x_{\mu,A}, \dots, x_{\mu,J}, \dots, x_{\mu,N-1}, x_{\mu,su})$ . Even by considering only infinitesimal perturbations of the composition, the complete solution of the mathematical problem is only possible if the eluent contains not more than two components (*i.e.*, the eluent is a binary mixture). In this case the retention volume of an infinitesimal perturbation of the concentration vector is given by

$$V_{R,i} = v_{\mu}^0 \left[ \left( \frac{\partial n_{\kappa,i}}{\partial x_{\mu,i}} \right)_{\bar{x}_{\mu}^0} - x_{\mu,i}^0 \left( \frac{\partial n_{\kappa,tot}}{\partial x_{\mu,i}} \right)_{\bar{x}_{\mu}^0} \right] \tag{8}$$

where  $v_{\mu}^0 = v_{\mu}(\bar{x}_{\mu}^0)$  is the mean molar volume of the eluent and all other symbols are as previously defined. If  $i$  is a solute, its initial concentration  $x_{\mu,i}^0 = 0$  and eqn. 8 yields the retention volume in the usual sense. If a small sample of one of the components, A or B, of the binary eluent is injected, the resulting peak is called the "concentration peak" and its retention volume is designated as  $V_{R,cc}$ . As the composition of the binary eluent is given by only one independent variable [*i.e.*,  $\bar{x}_{\mu}^0 = (x_{\mu,A}^0)$  as  $x_{\mu,B} = 1 - x_{\mu,A}$ ] there will be only one concentration peak. In general, the injection of a solute will also perturb the concentration of the mixture, and therefore two peaks will appear: the peak of the solute and that of the concentration perturbation, as illustrated in Fig. 2.

With binary mixtures as eluent *eqn. 8 is a retention equation of general validity* for isothermal, isocratic analytical chromatography and the solution is independent of the retention mechanism. For the retention volume of solutes it is also valid in any

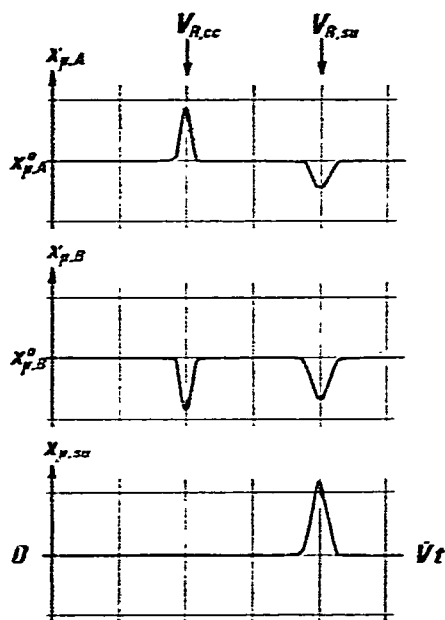


Fig. 2. Trace of a detector capable of measuring the concentration,  $\bar{x}_\mu(L,t)$  (molar fraction), after injection of a solute, su, in an eluent composed of a binary mixture with components A and B. Composition of the eluent before injection is designated by  $\bar{x}_\mu^0$ ;  $V_{R,cc}$  is the retention volume of the perturbation of the eluent composition;  $V_{R,su}$  is that of the solute;  $\bar{V}$  is the (constant) flow-rate of the eluent; and  $t$  is time. Note that  $x_{\mu,A} + x_{\mu,B} + x_{\mu,su} = 1$ .

N-component eluent. Its application to liquid–solid chromatography will be shown in a separate section.

In order to demonstrate its versatility, eqn. 8 will now be applied to a well known case: gas–liquid chromatography with a mobile phase composed of a mixture of two ideal gases; component S is soluble in the liquid stationary phase whereas component I is insoluble. The volume of the gas phase in the chromatographic column will be designated by  $V_\mu$ . Further, it is supposed that the liquid film on the inert solid support has the same density,  $d_\sigma$ , as that of the bulk. Therefore, the volume of the stationary phase can be calculated as  $V_\sigma = w_\sigma/d_\sigma$ , where  $w_\sigma$  is the mass of the stationary liquid in the column. The column capacity is then calculated as

$$n_{\kappa,J} = V_\mu c_{\mu,J} + V_\sigma c_{\sigma,J} = V_\mu x_{\mu,J}/v_\mu + V_\sigma c_{\sigma,J} \quad (9)$$

where  $v_\mu$  is the molar volume of the gas phase and J refers to one of the components of the mobile phase (I or S). The gas phase will always behave as a mixture of ideal gases such that  $v_\mu(\bar{x}_\mu^0) = v_\mu(\bar{x}_\mu) = RT_c/\bar{P}_c$ . Also, as component I is insoluble in the stationary phase, the column capacity is

$$n_{\kappa,\text{tot}} = V_\mu/v_\mu + V_\sigma c_{\sigma,S} \quad (10)$$

Eqn. 11 results from the use of eqns. 9 and 10 in eqn. 8 to calculate the retention volume:

$$V_{R,I} = V_{\mu} + V_{\sigma}(1 - x_{\mu,I}^0) v_{\mu} \left( \frac{\partial c_{\sigma,I}}{\partial x_{\mu,I}} \right)_{x_{\mu,I}^0} \quad (11)$$

This same result was found by Valentin and Guiochon<sup>16</sup> in their discussion of the "step and pulse method" for the determination of equilibrium isotherms (the "method of minor disturbance" in ref. 17). The reasoning used by these authors is, in principle, the same as that presented here, with the restriction that their treatment applies only to the specific case of gas chromatography.

Eqn. 11 gives the same retention volume for the perturbation of the eluent composition by the injection of a very small amount of S or I ("concentration peak", cc):

$$V_{R,cc} = V_{\mu} + V_{\sigma} v_{\mu} (1 - x_{\mu,S}^0) \left( \frac{\partial c_{\sigma,S}}{\partial x_{\mu,S}} \right)_{x_{\mu,S}^0} \quad (12)$$

expressed with  $x_{\mu,S}$  as the independent variable. Of course, the polarity of the detector signal will be inverted depending on whether S or I was injected. Eqn. 11 may be further applied to two special situations. In the first case, the concentration of the soluble gas,  $x_{\mu,S}^0$ , is diminished to a small value, small enough that  $(1 - x_{\mu,S}^0) \approx 1$  but much higher than the concentration perturbation introduced by a sample. For the injection of an "infinitesimal" amount of the insoluble carrier eqn. 12 gives the following for the retention volume of the "vacancy peak" (subscript vp; a special case of the concentration peak):

$$V_{R,vp} = V_{\mu} + V_{\sigma} v_{\mu} \left( \frac{\partial c_{\sigma,S}}{\partial x_{\mu,S}} \right)_{-0} = V_{\mu} + k_{S}^{(id*)} V_{\sigma}$$

where  $k_{S}^{(id*)}$  is the partition coefficient in the classical sense of the soluble gas, S, at ideal dilution, but, as the asterisk indicates, referring to a stationary phase saturated with the gas S. At these low concentrations eqn. 13 may be generalized. If the gas S is a mixture of  $n$  components,  $S_a, \dots, S_j, \dots, S_n$ , but the total concentration of the soluble gases remains small, then the injection of an even smaller amount of the insoluble carrier will provoke a "vacancy chromatogram" as a series of "negative" peaks<sup>18</sup>. Eqn. 13 is valid for the retention volume of every component,  $S_j$ , in this chromatogram. In the second special case there is only an insoluble carrier ( $x_{\mu,S}^0 = 0$ ) and the soluble carrier is injected as solute,  $su \equiv S$ . Eqn. 12 simplifies to

$$V_{R,su} = V_{\mu} + V_{\sigma} v_{\mu} \left( \frac{\partial c_{\sigma,S}}{\partial x_{\mu,S}} \right)_0 = V_{\mu} + k_{S}^{(id)} V_{\sigma} \quad (14)$$

and gives the classical relationship for partition chromatography as presented by Martin and Syngé<sup>19</sup>. Eqn. 14 can also be generalized for an  $n$ -component sample of solutes. Comparing eqns. 13 and 14 it is seen that a "vacancy chromatogram" is the mirror image reflected through the baseline of that made in the normal mode if  $k^{(id*)} = k^{(id)}$ .

In summary, this section has shown that the chromatographic process can be described in terms of the column capacities,  $\bar{n}_k$ , and the composition of the mobile phase,  $\bar{x}_\mu$ . The composition vector is known and its deviation around the constant eluent composition,  $\bar{x}_\mu^0$ , is measured by a detector subsequent to the chromatographic column. On the other hand, for the measurement of the unknown column capacity only a non-chromatographic method was available, namely to empty the mobile phase from the column and then determine amount and composition of the column yield.

#### CHROMATOGRAPHIC DETERMINATION OF THE COLUMN CAPACITY

Let us imagine a solute,  $J^*$ , which is in every respect identical with component  $J$  of the eluent with the exception of one property permitting its detection. Obviously the two compounds are inseparable and the same molar ratio will be found everywhere in any system. In the chromatographic column, the following holds true:

$$\frac{n_{k,J^*}}{n_{k,J}} = \frac{x_{\mu,J^*}}{x_{\mu,J}} \left( = \frac{p_{\mu,J^*}}{p_{\mu,J}} = \frac{\varphi_{\mu,J^*}}{\varphi_{\mu,J}} \right) \quad (15)$$

The retention volume of the labelled component  $J^*$  can be calculated with eqn. 8 by substituting the partial derivative computed with the aid of eqn. 15. This results in

$$V_{R,J^*} = t_\mu^0 \left( \frac{\partial n_{k,J^*}}{\partial x_{\mu,J^*}} \right) \bar{x}_\mu^0 = t_\mu^0 n_{k,J}^0 \cdot x_{\mu,J}^0 \quad (16)$$

Rearrangement of eqn. 16 gives the relationship between molar component capacity, total molar eluent capacity and retention volumes of the labelled components as follows:

$$n_{k,J}^0 = x_{\mu,J}^0 V_{R,J^*} / t_\mu^0 \quad (17)$$

$$n_{k,tot}^0 = \sum_{J=A}^N (x_{\mu,J}^0 V_{R,J^*} / t_\mu^0) \quad (18)$$

Eqn. 18 gives the method of determination of the molar total eluent capacity of the column.

Following the suggestion of Knox and co-workers, for chromatographic purposes labelled solutes can best be approximated by compounds containing radioactive carbon<sup>8</sup>. Less satisfactory but much easier to work with regarding handling and detection are deuterated compounds proposed in ref. 20 and used by McCormick and Karger<sup>6,7</sup>. The best solution might be the use of a series of compounds with a different degree of deuteration. In general there is a small change in physical properties with the degree of deuteration from non-deuterated to fully deuterated compounds. To a first approximation, this change may be considered to be linear. Therefore, retention volumes of compounds deuterated to different degrees, e.g., 50 and 100%, could be extrapolated to 0% to give retention volumes of "labelled but not deuterated compounds".



ADSORPTION AT A LIQUID-SOLID INTERFACE

In the *classical experiment* demonstrating adsorption at a liquid-solid interface, a total of  $n_{\tau, \text{tot}}$  moles of an  $N$ -component liquid mixture of known composition  $\bar{x}_\tau$  is brought into contact with a solid of surface area  $S$ . After equilibration there remains a liquid phase, the composition of which is determined at a point far enough from the interface to give  $\bar{x}_\beta$  ( $\beta$  refers to the bulk). Any difference between the molar fraction of a component before and after contact,  $\Delta x_J = x_{\tau, J} - x_{\beta, J}$ , is interpreted to be the effect of adsorption of the components of the mixture at the liquid-solid interface. It is concluded that there is a surface phase in which material is retained with a composition different from that of the bulk but it is now realized that the information,  $n_{\tau, \text{tot}}$ ,  $\bar{x}_\tau$  and  $\Delta \bar{x}$ , is not sufficient to calculate the amount and composition of the adsorbed substance. Therefore, surface concentrations cannot be given.

Let us recall *Gibbs' proposal* to find the way out of this dilemma. For the description of the adsorption system in equilibrium a volume with a boundary parallel to the plane (not curved) interface,  $V_{\beta, \text{CX}}$ , is chosen for the liquid bulk by some well defined "convention X" (referred to by the subscript "CX"). The plane placed parallel to the interface to limit the bulk is normally termed the "Gibbs dividing plane". It is assumed that material in this volume has the bulk composition,  $\bar{x}_\beta$ . Volume and composition determine the material content of the bulk  $n_{\beta, J}$ , and as the total amount of component  $J$  in the system,  $n_{\tau, J}$ , is known, the adsorbed material,  $n_{\sigma, J}$ , can be calculated as in eqn. 19a. Further, being proved by experiment that the imbalance of the composition is proportional to the surface area of the solid, the following material balance can be written for each component:

$$n_{\sigma, J} = S\Gamma_{J, \text{CX}} = n_{\tau, J} - \bar{x}_{\beta, J} V_{\beta, \text{CX}} / v_{\beta}(\bar{x}_\beta) \quad (J = A, B, \dots, N) \quad (19a)$$

The *surface concentration*,  $\Gamma_{J, \text{CX}}$ , as defined by eqn. 19a and given in units of moles per unit surface area, clearly depends on the choice of the bulk volume and *can be positive or negative*.

Analogous reasoning can be applied in describing the adsorption process in terms of mass  $m$  and mass fraction  $p$ , resulting in surface concentrations  $\Pi$ , expressed in units of mass/surface area. The resulting material balance can also be obtained by multiplication of eqn. 19a with the molar mass,  $M_J$ , of component  $J$ , giving

$$m_{\sigma, J} = n_{\sigma, J} M_J = S\Pi_{J, \text{CX}} = m_{\tau, J} - p_{\beta, J} V_{\beta, \text{CX}} / \bar{v}_\beta(\bar{p}_\beta) \quad (19b)$$

where  $\bar{v}_\beta(\bar{p}_\beta) = v_\beta(\bar{x}_\beta) / M_\beta$  is the specific volume of the mixture in the bulk at the composition  $\bar{p}_\beta$  ( $M_\beta$  is the mean molar mass of the bulk).

Multiplication of eqn. 19a by the partial molar volume,  $v_J(\bar{x}_\beta)$ , of component  $J$  results in a similar material balance in terms of volume,  $V$ , volume fraction,  $\phi$ , and surface concentration,  $\Psi$ , in units of volume/surface area given by eqn. 19c:

$$V_{\sigma, J} = v_J(\bar{\phi}_\beta) n_{\sigma, J} = S\Psi_{J, \text{CX}} = V_{\tau, J}(\bar{\phi}_\beta) - \phi_{\beta, J} V_{\beta, \text{CX}} \quad (19c)$$

The language of eqn. 19c is unusual in application of Gibbs' procedure. Its basic drawback lies in the fact that partial volumes, being functions of the composition,

pressure and temperature, are also different in an adsorbed state. The value of a partial volume will change with the concentration gradient generated by the force field near the interface and its (average) value in the surface phase will not be known. In the adsorption system only the bulk has a well defined composition and there is no other choice but to refer to a partial volume at the bulk composition after the adsorption process ( $\bar{v}_B$ ). In conclusion, all disadvantages of this language originate from the "non-ideality" of fluid mixtures. Concerning volumes, however, the laws of ideal mixtures are in general good approximations for non-ionic liquid mixtures. Therefore, apart from some drawbacks, this language has several advantages. Surface concentrations expressed as volume per unit surface area are easy to visualize. In Figs. 3–5 these units are chosen to illustrate the principle of Gibbs' procedure. With the example of a binary (ideal) liquid mixture it is illustrated in Fig. 3 that surface concentrations depend directly on the position of the dividing plane, *i.e.*, on the volume attributed to the bulk.

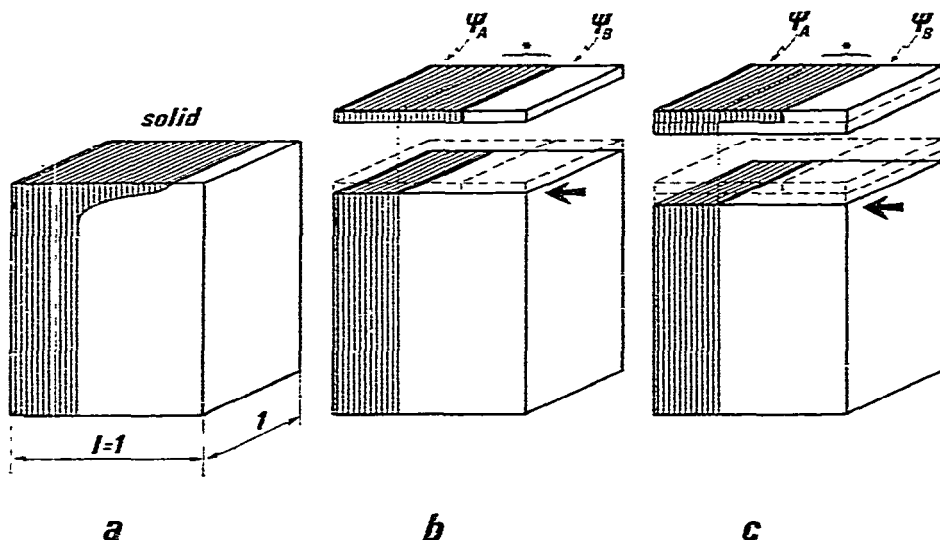


Fig. 3. Illustration of the adsorption in a binary liquid mixture at the interface in contact with a solid (above the liquid, not shown). (a) Near the interface there is a concentration gradient. (b), (c) A plane is placed parallel to the surface at two different positions chosen by purely arbitrary conventions. The portion cut off is considered as the surface phase accounting for the whole concentration difference near the surface. The bulk has now a well defined volume,  $V_B$ , and, being homogeneous, a well defined material content,  $V_B(c_{j,A} + c_{j,B})$ . The position of the plane (arrow) determines also the volumes of A and B left in the surface phase which, projected to the surface area of the dividing plane, give surface concentrations in units of volume/surface area. Note that the surface concentration of components  $\psi_A$  and  $\psi_B$  strongly depend on the position of the dividing plane. For the volume designated by an asterisk, see caption to Fig. 4.

The question now arises of how to fix the position of the Gibbs' dividing plane, and more specifically, how to fix it by an internal convention. Internal conventions are those which refer to the adsorption process itself. In the present treatment surface concentrations will only be referred to "classical" internal conventions. For an N-component mixture there are N conventions stating that component "J is not ad-

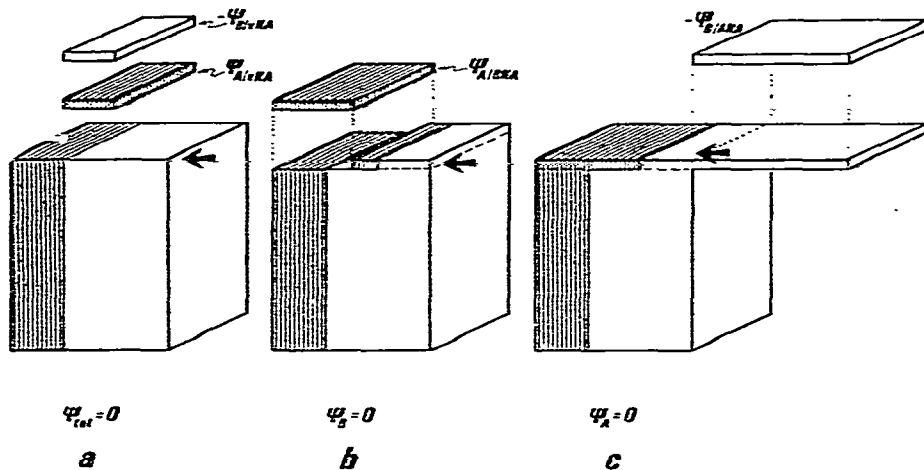


Fig. 4. Illustration of the surface concentration of adsorbed components,  $\Psi$  (volume/surface area), for three of the "classical" conventions to fix the position of the Gibbs dividing plane at the liquid-solid interface of a binary liquid mixture. The solid is above the liquid (not shown, as in Fig. 3). The component A is the more strongly adsorbed component while B exhibits a weaker adsorption. Note that for the sake of demonstration, the additional volume is not spread over the liquid surface (as it should be), extending the homogeneous liquid column up to the dividing plane the approximate position of which is marked by arrow. The excess concentration referring to the rNA convention is also identified in Fig. 3 (see in Fig. 3 the volume designated by an asterisk).

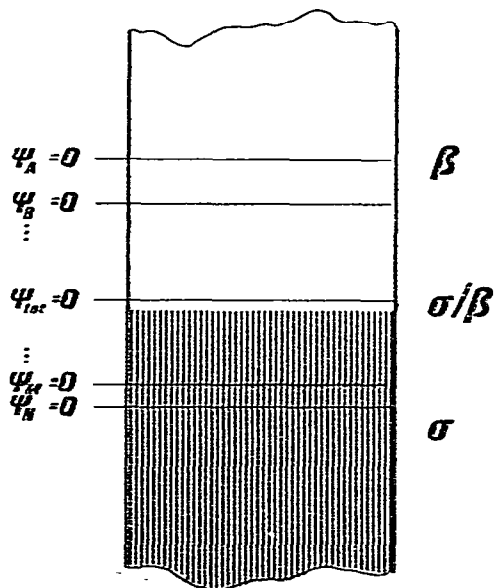


Fig. 5. "Classical" positions of the Gibbs dividing plane at the solid-liquid ( $\sigma/\beta$ ) interface of an  $N$ -component liquid mixture defined by the conditions indicated. Concentration of components in the surface phase,  $\Psi_A, \dots, \Psi_N$ , are given in units of volume/surface area. The component adsorbed weakest is A and adsorption strength is increasing to  $N$ . The bulk volume is largest (exceeding into the solid) if the plane is placed with the convention that the strongest adsorbed component is considered to be non adsorbed ( $\Psi_N = 0$ ) and smallest with the condition  $\Psi_A = 0$ . Note that with the condition that as an overall effect there is no adsorbed volume ( $\Psi_{tot} = 0$ ), the dividing plane is near the physical interface.

TABLE I

SUMMARY OF THE RELATIONSHIPS (A) FOR THE INTERPRETATION OF RETENTION VOLUMES IN LIQUID-SOLID CHROMATOGRAPHY WITH AN  $N$ -COMPONENT LIQUID MIXTURE AS THE ELUENT AND (B) FOR THE DETERMINATION OF ADSORPTION ISOTHERMS AT THE LIQUID-SOLID INTERFACE OF BINARY LIQUID MIXTURES BY THE CHROMATOGRAPHIC METHOD

The symbols  $\Gamma$ ,  $\Pi$  and  $\Psi$  represent surface concentrations in units of  $\text{mol m}^{-2}$ ,  $\text{g m}^{-2}$  and  $\text{ml m}^{-2}$ , respectively, and  $x$ ,  $p$  and  $\varphi$  are the corresponding dimensionless bulk concentrations: molar fraction, mass fraction and volume fraction. Lower-case Greek letters refer to material transported by the eluent being in the mobile phase,  $\mu$ , in the stationary phase,  $\sigma$ , or referring to the total capacity of the column ( $\kappa = \mu + \sigma$ ); in the static adsorption system  $\sigma$  has the same meaning and  $\beta$  refers to the bulk ( $\tau = \beta + \sigma$ ). Capital J or K refers to components of the eluent, su to a solute and cc to a concentration perturbation of the eluent. The symbols  $n$ ,  $m$  and  $v$  represent the number of moles, mass and volume, respectively;  $v$  is the partial molar volume and  $\bar{v}$  is the partial specific volume. An example for the interconversion of surface concentrations:  $\Gamma_{J, nNA}$  is to be converted to  $\Pi_{J, mNA}$ : calculate first  $\Gamma_{J, nNA} \cdot M_J = \Pi_{J, nNA}$  (mass concentration but with the incoherent convention) and substitute this into eqn. 24b. Interconversion in the JNA convention is simple, e.g.,  $\Pi_{K, JNA} = M_K \Gamma_{K, JNA}$ .

Convention		Gibbs' conventions for the adsorption from an $N$ -component liquid mixture at the liquid-solid interface; static system		Relationships for the interpretation of retention volumes in liquid-solid chromatography.	
Definition		Equations for the calculation and interconversion of surface concentrations referring to a "classical" convention		Exptl. detn. of $V_{R, K*}$	
	CY		Volume of the bulk, $V_{\beta, CY}$		
$\Gamma_J = \Pi_J = \Psi_J = 0$ *JNA (20)		$\Gamma_{K, JNA} = \Gamma_{K, CX} - (x_{\beta, K}/x_{\beta, J}) \Gamma_{J, CX}$ (22)	$n_{L, J} \bar{v}_{\beta, J}$ (26)	$V_{R, J*}$ (32)	
$\Gamma_{tot} = 0$	$nNA$ (23a)	$\Gamma_{J, nNA} = \Gamma_{J, CX} - x_{\beta, J} \sum_{K=A}^N \Gamma_{K, CX}$ (24a)	$v_{\beta} \sum_{K=A}^N n_{L, K}$ (27a)	$\sum_{K=A}^N x_{R, K}^0 V_{R, K*}$ (38a)	
$\Pi_{tot} = 0$	$mNA$ (23b)	$\Pi_{J, mNA} = \Pi_{J, CX} - p_{\beta, J} \sum_{K=A}^N \Pi_{K, CX}$ (24b)	$\bar{v}_{\beta} \sum_{K=A}^N m_{L, K}$ (27b)	$\sum_{K=A}^N p_{R, K}^0 V_{R, K*}$ (38b)	
$\Psi_{tot} = 0$	$vNA$ (23c)	$\Psi_{J, vNA} = \Psi_{J, CX} - \varphi_{\beta, J} \sum_{K=A}^N \Psi_{K, CX}$ (24c)	$\sum_{K=A}^N n_{L, K} \bar{v}_K$ (27c)	$\sum_{K=A}^N \varphi_{R, K}^0 V_{R, K*}$ (38c)	

\* Note that  $\Pi_{K, JNA} = M_K \Gamma_{K, JNA}$  and  $\Psi_{K, JNA} = v_K \Gamma_{K, JNA}$ .

\*\* Valid for ideal mixtures only. For real mixtures see eqn. 94 in the Appendix.

sorbed". This JNA convention, as introduced, is independent of the units used, contrary to a further "nothing is adsorbed" NA convention. In this further case it is construed to fix the total amount adsorbed as zero in terms of number of moles ( $n$ ) or mass ( $m$ ) or volume ( $v$ ). Consequently, there will be only one JNA convention but three different NA conventions:  $nNA$ ,  $mNA$  and  $vNA$ .

In order to show that these conventions allow the calculation of well defined surface concentrations, let us suppose that surface concentrations referring to an

*Experimental determination of points on the isotherm of A in a binary mixture, A + B*

Const. of eqn. 43, $v_\mu$	Peak propagation resistivity, $\lambda_{i\text{CX}}$ in eqn. 43	Labelled K	Solute	Concentration peak $\chi_{\text{CX}}$	Isotherm of A: $\Gamma_A, \Pi_A$ and $\Psi_A$ from experiment		
$\Gamma_\mu^0$	$\left(\frac{\Gamma_{K/JNA}^0}{x_{\mu,K}}\right)$	(33)	$\left(\frac{\partial \Gamma_{su/JNA}}{\partial x_{\mu,su}}\right)_{\bar{x}_\mu^0}$	(34)	$\left(\frac{\partial \Gamma_{A/BNA}}{\partial x_{\mu,A}}\right)_{x_{\mu,A}^0}$	(35) $x_{\mu,A}^0 V_{N,A*} / S \Gamma_\mu^0$	(33)
$\Gamma_\mu^0$	$\left(\frac{\Gamma_{K/BNA}^0}{x_{\mu,K}}\right)$	(36a)	$\left(\frac{\partial \Gamma_{su/mNA}}{\partial x_{\mu,su}}\right)_{\bar{x}_\mu^0}$	(39a)	$\left(\frac{\partial \Gamma_{A/mNA}}{\partial x_{\mu,A}}\right)_{x_{\mu,A}^0}$	(40a) $\frac{(V_{R,A*} - V_{R,B*}) x_{\mu,A}^u x_{\mu,B}^u}{S \Gamma_\mu^0}$	(45a)
$\bar{\Gamma}_\mu^0$	$\left(\frac{\Pi_{K/mNA}^0}{p_{\mu,K}}\right)$	(36b)	$\left(\frac{\partial \Pi_{su/mNA}}{\partial p_{\mu,su}}\right)_{\bar{p}_\mu^0}$	(39b)	$\left(\frac{\partial \Pi_{A/mNA}}{\partial p_{\mu,A}}\right)_{p_{\mu,A}^0}$	(40b) $\frac{(V_{R,A*} - V_{R,B*}) p_{\mu,A}^0 p_{\mu,B}^0}{S \bar{\Gamma}_\mu^0}$	(45b)
1	$\left(\frac{\Psi_{K/cNA}^0}{\varphi_{\mu,K}}\right)$	(36c)	$\left(\frac{\partial \Psi_{su/cNA}}{\partial \varphi_{\mu,su}}\right)_{\bar{\varphi}_\mu^0}$	(39c)	$\left(\frac{\partial \Psi_{A/cNA}}{\partial \varphi_{\mu,A}}\right)_{\varphi_{\mu,A}^0}^{**}$	(40c) $\frac{(V_{R,A*} - V_{R,B*}) \varphi_{\mu,A}^0 \varphi_{\mu,B}^0}{S}$	(45c)

arbitrary convention, CX, are known. For a first example, it is presumed that

$$\Gamma_j = 0 (= \Pi_j = \Psi_j) \tag{20}$$

implementing the JNA convention in the  $n-x-\Gamma$  language. The link between surface concentrations referring to the CX and JNA conventions is formed by applying eqn. 19a successively to calculate  $\Gamma_{K/CX}$ ,  $\Gamma_{K/JNA}$  and  $\Gamma_{J/JNA} (= 0)$ . Combination of the

resulting expressions gives, after rearrangement, eqn. 21,

$$\Gamma_{K/JNA} = \Gamma_{K/CX} - (x_{\beta,K}/x_{\beta,J}) [n_{r,J} - x_{\beta,J} V_{\beta,CX}/v_{\beta}(\bar{x}_{\beta})] S \quad (21)$$

Comparison of eqn. 21 with eqn. 19a reveals that the coefficient of  $(x_{\beta,K}/x_{\beta,J})$  is the surface concentration  $\Gamma_{J/CX}$  and so

$$\Gamma_{K/JNA} = \Gamma_{K,CX} - (x_{\beta,K}/x_{\beta,J}) \Gamma_{J,CX} \quad (22)$$

Eqn. 22 can be multiplied by  $M_K$ , the molar mass of component K, or by its partial molar volume,  $v_K(\bar{x}_{\beta})$ , to give analogous expressions in terms of the variables  $p$ ,  $\Pi$  and  $\varphi$ ,  $\Psi$  without changing the convention.

To give "excess adsorption" or "reduced adsorption" in terms of number of moles the convention "nothing is adsorbed" ( $nNA$  convention) is given by

$$\Gamma_{tot} = \sum_{J=A}^N \Gamma_J = 0 \quad (\neq \Pi_{tot} \neq \Psi_{tot}) \quad (23a)$$

Similar reasoning to that leading to eqn. 22 gives, by using eqn. 23a in 19a, the surface concentration of component J:

$$\Gamma_{J,nNA} = \Gamma_{J,CX} - x_{\beta,J} \sum_{K=A}^N \Gamma_{K,CX} = \Gamma_{J,CX} - x_{\beta,J} \Gamma_{tot,CX} \quad (24a)$$

Analogous equations in terms of the variables  $m$ - $p$ - $\Pi$  and  $v$ - $\varphi$ - $\Psi$  with the conventions "mNA" and "vNA" are listed in Table I (eqns. 24b and c). Eqns. 24a, b and c imply that surface concentration and NA convention should be coherent meaning that the convention should be stated in units coherent with that of the surface concentration. Consequently, only  $\Gamma_{J,nNA}$ ,  $\Pi_{J,mNA}$  and  $\Psi_{J,vNA}$  are *surface concentrations with coherent conventions*. Incoherent surface concentrations are obtained in equations of the following type:

$$\Gamma_{J,nNA} M_J = \Pi_{J,mNA} \quad (25)$$

where  $M_J$  is the molecular mass of J. Obviously, the mass surface concentration in eqn. 25 refers to the  $nNA$  convention and can be substituted into eqn. 24b to be converted to  $\Pi_{J,mNA}$  with the coherent convention if the surface concentrations of all components are known in the  $nNA$  convention. Sometimes incoherent surface concentrations are encountered in the literature (see, e.g.,  $\Gamma_{J,vNA}$  in refs. 7 and 11).

Surface concentrations defined in eqns. 24 and 26 are independent of the position of the Gibbs dividing plane. Alternatively, these surface concentrations are true surface concentrations for a particular position of the dividing plane fixed by the convention which is characterized by the condition stated in the convention (e.g.,  $\Gamma_J = 0$  for the JNA convention or  $\Psi_{tot} = 0$  for the vNA convention, etc.). Fig. 4 illustrates the three "classical" positions of the Gibbs dividing plane for a binary mixture and Fig. 5 the  $N+1$  positions of this plane for an  $N$ -component mixture where conventions are stated in terms of concentrations expressed in  $v$ - $\varphi$ - $\Psi$  units. It can be seen

that the dividing plane is inside the liquid mixture if the adsorption is expressed relative to that of the weaker adsorbed substance and inside the solid if the stronger adsorbed substance is the standard. For the following discussion note that in practice the plane corresponding to the  $v$ NA convention is very near to the physical surface of the liquid.

The calculation of the bulk volume corresponding to a given convention is straightforward. For an example, applying the JNA convention expressed in eqn. 20 to eqn. 19a gives

$$V_{\beta;JNA} = v_{\beta}(\bar{x}_{\beta}) n_{\tau,J} / x_{\beta,J} \tag{26}$$

where  $V_{\beta;JNA}$  designates the value of the bulk phase volume with reference to the convention. The bulk volume corresponding to the  $n$ NA convention is obtained by summing eqn. 19a over all components in the system to give, after rearrangement

$$V_{\beta;nNA} = v_{\beta}(\bar{x}_{\beta}) \sum_{J=A}^N n_{\tau,J} \tag{27a}$$

where the symbol  $V_{\beta;nNA}$  stands for the volume of the bulk with reference to this specific convention and the units used to introduce the convention. Bulk volumes referring to other conventions are listed in Table I.

In summarizing Gibbs' procedure, let us emphasize three points before applying the results to liquid–solid chromatography:

(a) Surface concentrations  $\Gamma_{J,CX}$ ,  $\Pi_{J,CX}$  and  $\Psi_{J,CX}$  are intensive equilibrium properties of the adsorption system and so at a given temperature and pressure they are functions of the bulk composition only:

$$\Gamma_{J,CX} = \Gamma_{J,CX}(\bar{x}_{\beta}) \quad (\text{mol/surface area}) \tag{28a}$$

$$\Pi_{J,CX} = \Pi_{J,CX}(\bar{p}_{\beta}) \quad (\text{mass/surface area}) \tag{28b}$$

$$\Psi_{J,CX} = \Psi_{J,CX}(\bar{q}_{\beta}) \quad (\text{volume/surface area}) \tag{28c}$$

As already mentioned, units for convention and surface concentration should be coherent and should refer to one of the three systems: the  $n$ - $x$ - $\Gamma$  system of molar units (referred to by the subscript  $n$ ), the  $m$ - $p$ - $\Pi$  system of mass units ( $m$ ) or the  $v$ - $\varphi$ - $\Psi$  system of volume units ( $v$ ).

(b) Bulk volume,  $V_{\beta;CX}$ , has the dimensions of volume but is a convention and has no physical meaning. Its value depends on the total number of moles,  $\bar{n}_{\tau}$ , and on the composition of the bulk if the convention is internal.

(c) There is an important difference between the system in the classical adsorption experiment and that determined by the chromatographic column; in the latter case the overall volume of the liquid–solid system is imposed.

#### LIQUID–SOLID ADSORPTION CHROMATOGRAPHY

By identifying the composition of the "mobile phase" ( $\bar{x}_{\mu}$ ) in the chromatographic model with that of the "bulk liquid" ( $\bar{x}_{\beta}$ ), and the capacity vector of the chro-

matographic column ( $\bar{n}_\kappa$ ) with the vector of total number of moles in the adsorption system ( $\bar{n}$ ) the retention volume in liquid–solid chromatography is easy to calculate by use of eqn. 8. This derivation will be demonstrated by applying units related to number of moles,  $n$  (for analogous derivations in other units, see Appendix and Table I).

The molar component capacity of the column for any substance,  $i$ , is calculated using eqn. 19a ( $\beta \rightarrow \mu$ ;  $\tau \rightarrow \kappa$ ) to give, after rearrangement:

$$n_{\kappa,i} = x_{\mu,i} V_{\mu \text{ CX}} / v_{\mu}(\bar{x}_{\mu}) + S \Gamma_{i, \text{CX}} \quad (29)$$

By summing eqn. 29 over all components in the system, the molar total capacity is given by

$$n_{\kappa, \text{tot}} = V_{\mu \text{ CX}} / v_{\mu}(\bar{x}_{\mu}) + S \Gamma_{\text{tot}, \text{CX}} \quad (30)$$

Using eqns. 29 and 30 in eqn. 8, the retention volume of component  $i$  is calculated as

$$V_{R,i} = V_{\mu, \text{CX}}(\bar{x}_{\mu}^0) + S v_{\mu}^0 \left[ \left( \frac{\partial \Gamma_{i, \text{CX}}}{\partial x_{\mu,i}} \right)_{\bar{x}_{\mu}^0} - x_{\mu,i}^0 \left( \frac{\partial \Gamma_{\text{tot}, \text{CX}}}{\partial x_{\mu,i}} \right)_{\bar{x}_{\mu}^0} \right] \quad (31)$$

Let us now apply eqn. 31 to the three cases important for analytical chromatography: the retention volume of labelled components of the eluent, of the concentration peak (binary eluent) and of solutes.

With the convention "J is not adsorbed" (J is a component of the eluent), eqn. 31 gives for labelled J:

$$V_{R,J*} = V_{\mu/JNA} \quad (32)$$

giving the experimental method for the determination of  $V_{\mu/JNA}$ . For labelled K, the following equation results;

$$V_{R,K*} = V_{\mu/JNA} + S v_{\mu}^0 \left( \frac{\Gamma_{K/JNA}^0}{x_{\mu,K}^0} \right) \quad (33)$$

For a solute the following equation results:

$$V_{R,su} = V_{\mu/JNA} + S v_{\mu}^0 \left( \frac{\partial \Gamma_{su/JNA}}{\partial x_{\mu,su}} \right)_{\bar{x}_{\mu}^0} \quad (34)$$

Injection of a solute always perturbs the eluent concentration, and therefore the peak given in eqn. 34 will always be accompanied by (one or more) concentration peaks (probably there will be  $N-1$  concentration peaks<sup>4</sup>). In a binary eluent, eqn. 31 gives for the perturbation of the concentration ( $J \equiv B$ ) "a concentration peak"<sup>17,21</sup> with the retention volume given by eqn. 35:

$$V_{R,cc} = V_{\mu/BNA} + S v_{\mu}^0 \left( \frac{\partial \Gamma_{A/BNA}}{\partial x_{\mu,A}} \right)_{\bar{x}_{\mu,A}^0} \quad (35)$$



With the convention "nothing is adsorbed" eqn. 31 reduces to a particularly simple form. Considering that by definition  $\Gamma_{101, nNA} = 0$ , eqn. 31 is transformed into

$$V_{R,i} = V_{\mu/nNA} + S v_{\mu}^0 \left( \frac{\partial \Gamma_{i, nNA}}{\partial x_{\mu,i}} \right) \bar{x}_{\mu}^0 \quad (36a)$$

For labelled J eqn. 36 gives

$$V_{R,J*} = V_{\mu, nNA} + S v_{\mu}^0 \left( \frac{\Gamma_{J, nNA}^0}{x_{\mu, J}^0} \right) \quad (37)$$

Multiplication of eqn. 37 by  $x_{\mu, J}$  and summing the N equations gives the experimental method for the determination of the volume,  $V_{\mu, nNA}$ , referring to this convention:

$$V_{\mu/nNA} = \sum_{J=A}^N x_{\mu, J}^0 V_{R,J*} \quad (38a)$$

Application of eqn. 36 to a solute gives

$$V_{R,su} = V_{\mu/nNA} + S v_{\mu}^0 \left( \frac{\partial \Gamma_{su/nNA}}{\partial x_{\mu, su}} \right) \bar{x}_{\mu}^0 \quad (39a)$$

Finally, the retention volume of a concentration peak in a binary mixture is given by

$$V_{R,cc} = V_{\mu/nNA} + S v_{\mu}^0 \left( \frac{\partial \Gamma_{A' nNA}}{\partial x_{\mu, A}} \right) x_{\mu, A}^0 \quad (40a)$$

The derivations followed in eqns. 31–36–40 were repeated, *mutatis mutandis*, with the  $p^*$  and  $vNA$  conventions. The results are listed in Table I.

The general form of the equation for liquid–solid chromatography is

$$V_{R,i} = V_{\mu/CX} (\bar{x}_{\mu}^0) + S v_{\mu} \chi_{i/CX} \quad (41)$$

where  $v_{\mu}$  is a property of the eluent and  $\chi_{i/CX}$  will be referred to as the *peak propagation resistivity* of the stationary phase in question for compound *i*.

It is interesting to compare this expression with the "classical" equation for the retention volume in partition chromatography given in eqn. 14. The first term in eqn. 41 is independent of the solute and therefore it will be interpreted as a "hold-up volume by convention". The second term is proportional to the surface area of the adsorbent, *S*, which has the same role as the volume of the stationary phase,  $V_{\sigma}$ , and finally the coefficient of *S* is analogous to the partition coefficient. Let us emphasize that these analogies are purely formal with the exception of that between *S* and  $V_{\sigma}$ . The hold-up volume is the result of a convention and therefore it has no physical meaning. Further, a partition coefficient can never become negative and  $\chi_{i/CX}$  in eqn. 41 can. However, it is right to designate the peak propagation resistivity of a solute as a Henry coefficient. It is now clear that "net retention volumes" can be defined by

analogy with classical partition chromatography as

$$V_{N,i,CX} = V_{R,i} - V_{\mu,CX} \quad (42)$$

but they will depend on the convention. Specific retention volumes should be referred to unit surface area of the adsorbent;

$$V_{S,i,CX} = V_{N,i,CX}/S = v_{\mu} \chi_{i,CX} \quad (43)$$

Equations listed in Table I give all the information necessary to determine the hold-up volume experimentally and to interpret retention volumes correctly with reference to a given convention.

It was repeatedly stressed that hold-up volumes are based purely upon conventions but the question now arises as to which hold-up volume is nearest to the "geometrical interstitial volume" of the column. Although at first sight real to some extent, this volume is also an undefined quantity, having no special convention to fix exactly the position of the dividing plane. Actually, the volume eluent capacity of the column measured with a pure liquid would be the geometrical interstitial volume if the density (specific volume) of the liquid in question was the same in the bulk and adsorbed state and if the boundary between liquid and solid was independent of the nature of the liquid. If these two conditions are fulfilled, the proposition of refs. 22 and 23 to calculate this volume from the weight difference of the column filled with two liquids and using the density of the pure non-adsorbed liquid in the calculations would result in the correct answer. An additional condition should be fulfilled if mixtures are used for its determination: the partial molar volumes of the components should remain the same at the composition of the surface phase as they are in the bulk. In practice, in non-ionic mixtures, partial molar volumes can be considered to be independent of composition to within 3%. It is therefore expected that the volume eluent capacity will also be a constant within these limits if the pore size of the solid is such that exclusion effects may be ignored.

#### DETERMINATION OF THE ADSORPTION ISOTHERM IN BINARY LIQUID MIXTURES

In the case of a binary eluent, composed of A and B, derivation of the necessary equations for the determination of the "composite isotherm" is straightforward.

In binary eluents there is only one independent variable of composition and points on this isotherm can easily be calculated from retention data of labelled A and B. For example, in the case of the molar "nothing is adsorbed" convention the sum of  $\Gamma_{A/nNA}$  and  $\Gamma_{B/nNA}$  is zero, and therefore

$$\Gamma_{B/nNA} = -\Gamma_{A/nNA} \quad (44)$$

Eqn. 37 applied to solutes A\* and B\* and the combination of the results with eqn. 44 produces, after rearrangement

$$\Gamma_{A/nNA}(x_{\mu,A}^0) = (V_{R,A^*} - V_{R,B^*})x_{\mu,A}^0 x_{\mu,B}^0/S v_{\mu}^0 \quad (45a)$$

By injection of labelled A or B a concentration peak is also produced, its net retention volume providing the first derivative of the isotherm as further information. Combination of eqns. 40 and 42 gives

$$\left(\frac{\partial \Gamma_{A/BNA}}{\partial x_{\mu,A}}\right)_{x_{\mu,A}^0} = V_{N,cc/BNA}/v_{\mu}^0 S \quad (46)$$

Complete information is given for isotherms expressed in other units in Table I.

The relationship of the retention volumes of labelled compounds and of the concentration perturbation to the composite isotherm in a binary mixture is illustrated in Fig. 6. The retention volumes were calculated for the two possible shapes of the composite isotherm, U- and S-shaped, using the volume/surface language and the convention  $\Psi_{tot} = 0$ .

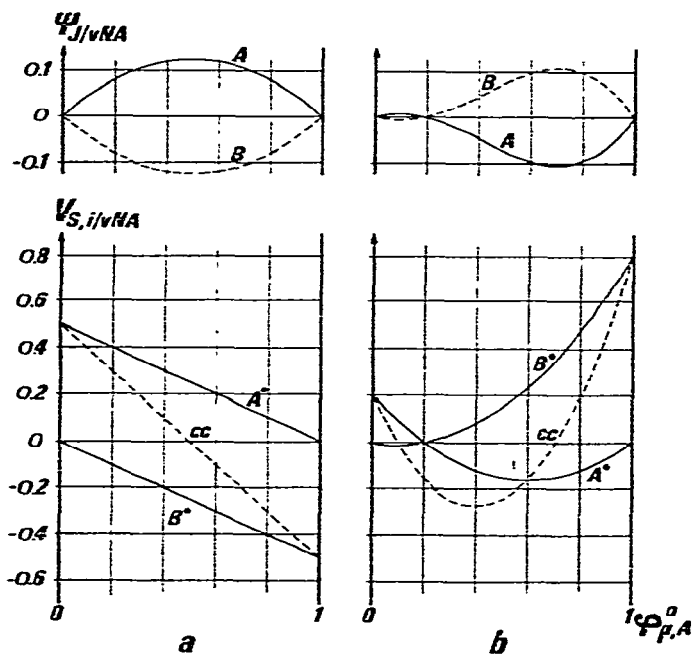


Fig. 6. Relationship between the composite isotherm of component A of a binary liquid mixture,  $\Psi_{A/BNA}$ , and the specific retention volumes of the labelled components,  $A^*$  and  $B^*$ , and the perturbation of the concentration,  $cc$ , if the ideal mixture of A and B is used as the eluent. The specific retention volume, designated by  $V_{S,i/vNA}$ , is the net retention volume referred to  $1 \text{ m}^2$  of adsorbent surface and to the specific condition  $\Psi_{tot} = 0$ . The example constructed employs arbitrary units but in practice figures of similar order of magnitude are obtained if expressing the data in units of  $\mu\text{l m}^{-2}$  ( $= \text{nm}$ ). (a) The equation used for the U-shaped isotherm is  $\Psi_{A/BNA} = \varphi_{\mu,A}^0 \varphi_{\mu,B}^0 / 2$ ; (b) the equation for the S-shaped isotherm is  $\Psi_{A/BNA} = \varphi_{\mu,B}^0 (0.2 - \varphi_{\mu,A}^0)$ .

CONCLUSION

The results of this discussion may be important in two areas. The first concerns the experimental determination of composite adsorption isotherms. By the classical

method, a given amount of a liquid mixture of known composition is equilibrated with a given amount of adsorbent and a point on the adsorption isotherm is calculated from the composition change. Experimentally, this method is relatively easy with powders with high-energy surfaces where the wetting angle is zero or very nearly so. Even in this case, equilibrium times of several hours are common. The chromatographic method might considerably reduce the time of the determination of the twenty or more experimental points necessary to describe the isotherm. Concerning hydrophobic, low-energy surfaces, this could be the only method for the determination of composite adsorption isotherms at surfaces not wettable by the liquid. In spite of wetting angles of up to  $100^\circ$  (water on paraffinic surfaces)<sup>24</sup>, even small mesopores would be completely filled at the pressures usually applied in liquid chromatography to establish the necessary contact between the liquid and the whole surface of the low-energy solid. For the calculation of isotherms, the experimental points must be evaluated in the coherent language of units and of a specific convention. Of course, one could create new conventions; the composite isotherm symbolized by  $\Gamma_{J;eNA}$  is given in units of  $\text{mol m}^{-2}$  but the position of the Gibbs dividing plane is determined by the requirement that the total adsorbed volume is zero and not the total adsorbed number of moles, and consequently  $\Sigma \Gamma_{J;eNA} \neq 0$ . Isotherms with such unusual conventions are described in refs. 7 and 11.

The second area is liquid-solid chromatography. Retention data have a definite meaning only if the hold-up volume is determined in the "self-consistent field" of the logic of the adsorption process. Of course, it would be desirable for data to be interconvertible. Actually they are, but only if detailed knowledge is available about the properties and adsorption behaviour of the components of the eluent, *i.e.*, if all the  $N-1$  independent isotherms are known. For the recording and publication of liquid chromatographic data there appears to be a serious problem of communication and two related questions must be asked: (a) what is the best language to be applied in the calculation of hold-up volumes?, and (b) what is the net retention volume in liquid chromatography?

The hold-up volume,  $V_{u;eNA}$ , has already been proposed and by Knox and co-workers<sup>8</sup> for general use. Indeed, in practice a hold-up volume that is easy to model would be advantageous and an approximately constant hold-up volume would be preferable in approximate calculations. These arguments point very strongly towards the convention "nothing is adsorbed" in terms of volume,  $V_{u;eNA}$ . Further, as already mentioned, this hold-up volume is nearest to some sort of geometrical interstitial volume in the column and it can also be approximated by the weighing method of refs. 22 and 23 if adsorbents of low surface energy are used, as in reversed-phase chromatography. On the other hand, theoretical arguments are in favour of the relative adsorption language with the "J is not adsorbed" convention, because in the Gibbs equation for adsorption from mixtures the decrease in the interfacial tension is proportional to this surface concentration.

An experimental verification of the results presented in this paper and further information on this subject will be published in the near future<sup>25</sup>.

## APPENDIX

### *Solution of the mass balance equation (eqns. 6-8)*

The law of mass conservation was expressed by a system of  $m$  partial differen-

tial equations (eqn. 6). Replacement of the  $m$ th of these equations by the sum of all equations gives the set

$$\begin{aligned} \frac{\partial}{\partial t} (n_{\kappa,i}/L) &= - \frac{\partial}{\partial z} (\dot{V} x_{\mu,i} / v_{\mu}) \quad (i = a, \dots, m-1) \\ \frac{\partial}{\partial t} (n_{\kappa,\text{tot}}/L) &= - \frac{\partial}{\partial z} (\dot{V} / v_{\mu}) \end{aligned} \quad (47)$$

In order to solve this system of equations, it is convenient to perform a change of variables, replacing the pair  $(z, t)$  by a new set of independent variables  $[z, q(z, t)]$  by using the following rules:

$$\begin{aligned} \left( \frac{\partial}{\partial t} \right)_z &= \left( \frac{\partial q}{\partial t} \right)_z \left( \frac{\partial}{\partial q} \right)_z \\ \left( \frac{\partial}{\partial z} \right)_t &= \left( \frac{\partial}{\partial z} \right)_q + \left( \frac{\partial q}{\partial z} \right)_t \left( \frac{\partial}{\partial q} \right)_z \end{aligned} \quad (48)$$

where the subscripts indicate in which set of variables the partial differentiations are performed. The new variable,  $q$ , is defined as

$$q(z, t) = \int_0^t (\dot{V} / v_{\mu}) dt \quad (49)$$

Eqn. 49 gives, after partial differentiation,

$$\left( \frac{\partial q}{\partial t} \right)_z = \dot{V} / v_{\mu} \quad (50)$$

The last equation of the set 47 can now be written as

$$\frac{\partial}{\partial t} (n_{\kappa,\text{tot}}/L) = - \frac{\partial^2 q}{\partial z \partial t} \quad (51)$$

As by definition  $q(z, t=0) = 0$  for all  $z$  (see eqn. 49), integration of eqn. 51 with respect to time gives

$$\left( \frac{\partial q}{\partial z} \right)_t = (n_{\kappa,\text{tot}}^0 - n_{\kappa,\text{tot}}) / L \quad (52)$$

where the superscript zero indicates that the function is taken at the initial time ( $t = 0$ ):

$$n_{\kappa,\text{tot}}^0 \equiv n_{\kappa,\text{tot}}(z, t=0) \quad (53)$$

The new variable  $q$  may be interpreted as a "local time", given at each distance,  $z$ ,

from the column inlet as the total number of moles having flowed through the cross-section from the beginning of the process ( $t=0$ ) to time  $t$ . The transformation of variables indicated in eqn. 48 applied to the first  $m-1$  equations of system 47, combined with eqns. 50 and 51, leads, after rearrangement, to

$$\frac{1}{L} \left[ \frac{\partial}{\partial q} (n_{\kappa,i} - x_{\mu,i} n_{\kappa,\text{tot}}) + n_{\kappa,\text{tot}}^0 \cdot \frac{\partial x_{\mu,i}}{\partial q} \right] = -\frac{\partial x_{\mu,i}}{\partial z} \quad (i = a, \dots, m-1) \quad (54)$$

As previously noted, the molar capacities,  $n_{\kappa,i}$ , depend only on the mobile phase composition  $\bar{x}_\mu$ :

$$n_{\kappa,i} = n_{\kappa,i} [\bar{x}_\mu(z,q)] \quad (55)$$

The system of  $m-1$  differential equations (eqn. 54) can now be written in the form

$$\frac{1}{L} \sum_{l=a}^{m-1} \left[ \frac{\partial}{\partial x_{\mu,l}} (n_{\kappa,i} - x_{\mu,i} n_{\kappa,\text{tot}}) + \delta_{il} n_{\kappa,\text{tot}}^0 \right] \frac{\partial x_{\mu,l}}{\partial q} = -\frac{\partial x_{\mu,i}}{\partial z} \quad (i = a, \dots, m-1) \quad (56)$$

where the Kronecker symbol,  $\delta_{il}$ , is defined as usual ( $\delta_{il} = 0$  if  $i \neq l$  and  $\delta_{il} = 1$  for all  $i$ ). With vector notation, the set of eqn. 56 becomes

$$A \cdot \frac{\partial \bar{x}_\mu}{\partial q} = -\frac{\partial \bar{x}_\mu}{\partial z} \quad (57)$$

where  $A$  is the  $(m-1) \times (m-1)$  matrix with the elements  $a_{il}$ :

$$a_{il}(\bar{x}_\mu) = \frac{1}{L} \left[ \frac{\partial}{\partial x_{\mu,l}} (n_{\kappa,i} - x_{\mu,i} n_{\kappa,\text{tot}}) + \delta_{il} n_{\kappa,\text{tot}}^0 \right] \quad (i, l = a, \dots, m-1) \quad (58)$$

If at time  $t = 0$  the composition of the mobile phase is uniform along the column, then

$$\bar{x}_\mu(z, t=0) = \bar{x}_\mu^0 \quad (59)$$

and if only infinitesimal perturbations of the concentration are considered, the matrix  $A$  can be taken as constant, its elements being  $a_{il}(\bar{x}_\mu^0)$ . Under the same assumptions, also the molar volume of the mobile phase is constant:

$$v_\mu(z,q) = v_\mu(x_\mu^0) \equiv v_\mu^0 \quad (60)$$

In this case the local time,  $q$ , is proportional to the volume having flowed through the cross-section, as follows from eqn. 49:

$$v_\mu^0 q(z,t) = \int_0^t \bar{V} dt \quad (61)$$

Let us now look for solutions of the system of eqns. 57 having the following particular form:

$$\bar{x}_\mu(z,q) = f_\lambda (\lambda z - q) \bar{x}_\mu^\lambda \tag{62}$$

where  $f_\lambda$  is any differentiable function and  $\bar{x}_\mu^\lambda$  is a constant vector. The calculation of partial derivatives of eqn. 62 is straightforward and gives

$$\begin{aligned} \frac{\partial \bar{x}_\mu}{\partial q} &= \frac{\partial f_\lambda}{\partial q} \cdot \bar{x}_\mu^\lambda \\ \frac{\partial \bar{x}_\mu}{\partial z} &= \frac{\partial f_\lambda}{\partial z} \cdot \bar{x}_\mu^\lambda = -\lambda \frac{\partial f_\lambda}{\partial q} \cdot \bar{x}_\mu^\lambda \end{aligned} \tag{63}$$

Introduction of eqn. 63 into the differential system 57 transforms it to an eigenvalue problem:

$$A \bar{x}_\mu^\lambda = \lambda \bar{x}_\mu^\lambda \tag{64}$$

An expression having the form of eqn. 64 is a solution of the differential problem if  $\lambda$  is an eigenvalue of the matrix  $A$  and  $\bar{x}_\mu^\lambda$  is the corresponding eigenvector. If the matrix  $A$  has  $(m-1)$  distinct eigenvalues  $(\lambda_a, \dots, \lambda_{m-1})$ , the set of the corresponding eigenvectors  $(\bar{x}_\mu^a, \dots, \bar{x}_\mu^{m-1})$  is a basis of the vector space of the  $\bar{x}_\mu$ . In this case the general solution of the differential problem may be written as a linear combination of the eigenvectors:

$$\bar{x}_\mu(z,q) = \sum_{i=a}^{m-1} f_i(\lambda_i z - q) \bar{x}_\mu^i \tag{65}$$

The coefficients  $f_i$  have to be determined from the boundary condition at the inlet of the column:

$$\bar{x}_\mu(z=0,q) = \bar{y}(q) \tag{66}$$

where  $\bar{y}(q)$  describes the composition of the mixture entering in the column as a function of the "local time",  $q(z=0,t)$ .

The form of eqn. 65 shows that, for any differentiable boundary condition (eqn. 66), the general solution is a superposition of  $m-1$  concentration signals, each traveling without deformation along the column with constant velocity (the inverse of the eigenvalue) with respect to the local time. Taking into consideration eqn. 61, the corresponding retention volumes are given as

$$V_{R,i} = v_\mu^0 \lambda_i L \quad (i = a, \dots, m-1) \tag{67}$$

Let us now examine the question of the existence of the eigenvalues of the matrix  $A$ , restricting the discussion to the case of a binary mixture as eluent, but allowing any number of solutes. Let  $a$  and  $m$  be the components of the eluent. For

each other substance in the system, the initial value of the molar fraction is zero by hypothesis:

$$x_{\mu,b}^0 = x_{\mu,c}^0 = \dots = x_{\mu,m-1}^0 = 0 \quad (68)$$

It is evident that if a substance has zero concentration in the mobile phase, its molar capacity in the column also disappears:

$$n_{\kappa,i}(\bar{x}_\mu) = 0 \quad (69)$$

if  $x_{\mu,i} = 0$ , whatever is the value of the other components of the vector  $\bar{x}_\mu$ . As a consequence the following rule is valid:

$$\left( \frac{\hat{c}n_{\kappa,i}}{\hat{c}x_{\mu,l}} \right)_{\bar{x}_\mu^0} = 0 \quad (70)$$

if  $i = b, c, \dots, m-1$  and  $l \neq i$ . The matrix  $A$  thus takes a triangular form, all elements  $a_{il}$  with  $l < i$  being zero; in fact, by eqn. 58 we have for  $i = b, \dots, m-1$  and  $l < i$ :

$$a_{il} = \frac{1}{L} \left[ \frac{\hat{c}}{\hat{c}x_{\mu,r}} (n_{\kappa,i} - x_{\mu,i} n_{\kappa,\text{tot}}) \right]_{\bar{x}_\mu^0} = 0 \quad (71)$$

The eigenvalues of a triangular matrix are the diagonal elements. If these eigenvalues are all distinct and positive, the signal observed at the outlet of the column will be a superposition of  $m-1$  signals characterized by the retention volumes given by eqn. 67:

$$\begin{aligned} V_{R,i} &= v_\mu^0 \left[ \left( \frac{\hat{c}}{\hat{c}x_{\mu,i}} (n_{\kappa,i} - x_{\mu,i} n_{\kappa,\text{tot}}) \right)_{\bar{x}_0} + n_{\kappa,\text{tot}}^0 \right] \\ &= v_\mu^0 \left[ \left( \frac{\hat{c}n_{\kappa,i}}{\hat{c}x_{\mu,i}} \right)_{\bar{x}_\mu^0} - x_{\mu,i}^0 \left( \frac{\hat{c}n_{\kappa,\text{tot}}}{\hat{c}x_{\mu,i}} \right)_{\bar{x}_\mu^0} \right] \quad (i = a, \dots, m-1) \end{aligned} \quad (72)$$

It should be noted that, depending on the boundary condition, some of these concentration signals may have a zero amplitude. It is easy to show that eqn. 72 (identical to eqn. 8) is also valid in an eluent composed of more than two components if  $i$  is a solute (i.e., if  $x_{\mu,i}^0 = 0$ ).

*Retention equations for liquid-solid chromatography in terms of different units; transformations of eqn. 31*

*Mass language:  $m$ - $p$ - $\Pi$  (mass, mass fraction, mass per unit surface area).* For a solute su ( $x_{\mu,\text{su}}^0 = 0$  or equivalently,  $p_{\mu,\text{su}}^0 = 0$ ), eqn. 31 reduces to

$$V_{R,\text{su}} = V_{\mu,\text{CX}} + S \cdot \frac{v_\mu^0}{M_{\text{su}}} \left( \frac{\partial \Pi_{\text{su/CX}}}{\hat{c}x_{\mu,\text{su}}} \right)_{\bar{x}_\mu^0} \quad (73)$$



By definition  $p_{\mu,i} = M_i x_{\mu,i} / M_\mu$ , so for a solute

$$\left( \frac{\hat{c} p_{\mu,su}}{\hat{c} x_{\mu,su}} \right)_{\bar{x}_\mu^0} = M_{su} / M_\mu^0 \quad (74)$$

On the other hand,  $\Pi_{su,CX}$  is identically zero if  $p_{\mu,su} = 0$ , and thus

$$\left( \frac{\hat{c} \Pi_{su,CX}}{\hat{c} x_{\mu,l}} \right)_{\bar{x}_\mu^0} = 0 \quad (75)$$

for  $l \neq su$ . Consequently, for solutes eqn. 76 holds true:

$$V_{R,su} = V_{\mu,CX} + S \bar{v}_\mu^0 \left( \frac{\hat{c} \Pi_{su,CX}}{\hat{c} p_{\mu,su}} \right)_{\bar{p}_\mu^0} \quad (76)$$

For the concentration peak, the derivation is restricted to the case of a binary mixture (A and B) as eluent. Eqn. 31 gives for the retention volume

$$V_{R,cc} = V_{\mu,CX} + S \bar{v}_\mu^0 \left[ \frac{x_{\mu,B}^0}{M_A} \left( \frac{d\Pi_{A,CX}}{dx_{\mu,A}} \right)_{x_{\mu,A}^0} - \frac{x_{\mu,A}^0}{M_B} \left( \frac{d\Pi_{B,CX}}{dx_{\mu,A}} \right)_{x_{\mu,A}^0} \right] \quad (77)$$

Differentiation of the expression  $p_{\mu,A} = M_A x_{\mu,A} / (M_A x_{\mu,A} + M_B x_{\mu,B})$  gives

$$\left( \frac{dp_{\mu,A}}{dx_{\mu,A}} \right)_{x_{\mu,A}^0} = M_A M_B / (M_\mu^0)^2 \quad (78)$$

Introduction of eqn. 78 into eqn. 77 gives, after rearrangement,

$$V_{R,cc} = V_{\mu,CX} + S \bar{v}_\mu^0 \left[ \left( \frac{d\Pi_{A,CX}}{dp_{\mu,A}} \right)_{p_{\mu,A}^0} - p_{\mu,A}^0 \left( \frac{d\Pi_{tot,CX}}{dp_{\mu,A}} \right)_{p_{\mu,A}^0} \right] \quad (79)$$

In particular, in the convention  $mNA$  ( $\Pi_{tot,mNA} = 0$ ) eqn. 79 simplifies to give

$$V_{R,cc} = V_{\mu,mNA} + S \bar{v}_\mu^0 \left( \frac{d\Pi_{A/mNA}}{dp_{\mu,A}} \right)_{p_{\mu,A}^0} \quad (80)$$

*Volume language:*  $v$ - $\varphi$ - $\Psi$  (*volume, volume fraction, volume per unit surface area*). For a solute  $su$  ( $x_{\mu,su}^0 = 0$  or equivalently  $\varphi_{\mu,su}^0 = 0$ ), eqn. 31 gives

$$V_{R,su} = V_{\mu,CX} + S \left[ \frac{v_\mu^0}{v_{su}^0} \left( \frac{\hat{c} \Psi_{su,CX}}{\hat{c} x_{\mu,su}} \right)_{\bar{x}_\mu^0} - \Gamma_{su,CX}(\bar{x}_\mu^0) \left( \frac{\hat{c} v_{su}}{\hat{c} x_{\mu,su}} \right)_{\bar{x}_\mu^0} \right] =$$

$$V_{\mu,CX} + S \cdot \frac{v_\mu^0}{v_{su}^0} \left( \frac{\hat{c} \Psi_{su,CX}}{\hat{c} x_{\mu,su}} \right)_{\bar{x}_\mu^0} \quad (81)$$

as  $\Gamma_{su,CX}(\bar{x}_\mu^0) = 0$ . By definition  $\varphi_{\mu,i} = v_i x_{\mu,i}/v_\mu$  ( $v_i$  is for the partial molar volume and  $v_\mu$  for the mean molar volume of the eluent), and so for a solute

$$\left(\frac{\hat{c}\varphi_{\mu,su}}{\hat{c}x_{\mu,su}}\right)_{\bar{x}_\mu^0} = v_{su}/v_\mu^0 \quad (82)$$

Considering that  $\Psi_{su,CX}$  is identically zero if  $\varphi_{\mu,su} = 0$ ,

$$\left(\frac{\hat{c}\Psi_{su,CX}}{\hat{c}\varphi_{\mu,l}}\right)_{\bar{\varphi}_\mu^0} = 0 \quad (83)$$

for  $l \neq su$ . Eqn. 81 can now be written as

$$V_{R,su} = V_{\mu,CX} + \left(\frac{\hat{c}\Psi_{su/CX}}{\hat{c}\varphi_{\mu,su}}\right)_{\bar{\varphi}_\mu^0} \quad (84)$$

The derivation for the concentration peak is restricted to a binary system. Eqn. 31 can be written in the following form:

$$V_{R,cc} = V_{\mu,CX} + S \left[ v_\mu^0 x_{\mu,B}^0 \left(\frac{d\Gamma_{A,CX}}{dx_{\mu,A}}\right)_{x_{\mu,A}^0} + v_\mu^0 x_{\mu,A} \left(\frac{d\Gamma_{B,CX}}{dx_{\mu,B}}\right)_{x_{\mu,A}^0} \right] \quad (85)$$

Let us now recall two basic properties of the molar volumes in a binary mixture:

$$\frac{dv_\mu}{dx_{\mu,A}} = v_A - v_B \quad (86)$$

$$\frac{dv_A}{dx_{\mu,A}} = x_{\mu,B} \frac{d^2 v_\mu}{dx_{\mu,A}^2} \quad (87)$$

and that the volume fraction  $\varphi_{\mu,A}$  is given by

$$\varphi_{\mu,A} = x_{\mu,A} v_A/v_\mu \quad (88)$$

By using eqns. 86 and 87 the derivative of the volume fraction with respect to the molar fraction can now be expressed as follows:

$$\frac{d\varphi_{\mu,A}}{dx_{\mu,A}} = \frac{v_A v_B}{v_\mu^2} + \frac{x_{\mu,A} x_{\mu,B}}{v_\mu} \frac{d^2 v_\mu}{dx_{\mu,A}^2} \quad (89)$$

As by definition  $\Psi_{A,CX} = v_A \Gamma_{A,CX}$ , the first term of the coefficient of  $S$  in eqn. 85 can be written as

$$v_\mu x_{\mu,B} \frac{d\Gamma_{A,CX}}{dx_{\mu,A}} = \frac{v_\mu x_{\mu,B}}{v_A} \left( \frac{d\Psi_{A,CX}}{d\varphi_{\mu,A}} \frac{d\varphi_{\mu,A}}{dx_{\mu,A}} - \Gamma_{A,CX} \frac{dv_A}{dx_{\mu,A}} \right) \quad (90)$$

Using eqns. 86, 87 and 88, the following expression is obtained after tedious manipulations:

$$v_{\mu} x_{\mu,B} \cdot \frac{d\Gamma_{A,CX}}{dx_{\mu,A}} = \varphi_{\mu,B}(1 + \alpha) \cdot \frac{d\Psi_{A,CX}}{d\varphi_{\mu,A}} - \alpha \cdot \frac{\varphi_{\mu,B}}{\varphi_{\mu,A}} \cdot \Psi_{A,CX} \quad (91)$$

where the parameter  $\alpha$  is

$$\alpha = (x_{\mu,A} x_{\mu,B} v_{\mu} / v_A v_B) \frac{d^2 v_{\mu}}{dx_{\mu,A}^2} \quad (92)$$

The value of  $\alpha$  remains unchanged if the subscripts A and B are interchanged. For reasons of symmetry a relation analogous to eqn. 91 is valid for the second term of the coefficient of  $S$  in eqn. 85:

$$v_{\mu} x_{\mu,A} \cdot \frac{d\Gamma_{B,CX}}{dx_{\mu,B}} = \varphi_{\mu,A}(1 + \alpha) \cdot \frac{d\Psi_{B,CX}}{d\varphi_{\mu,B}} - \alpha \cdot \frac{\varphi_{\mu,A}}{\varphi_{\mu,B}} \cdot \Psi_{B,CX} \quad (93)$$

Introduction of eqns. 91 and 93 into eqn. 85 gives the desired retention volume. Its form becomes particularly simple if the  $v_{NA}$  convention is chosen for the adsorption. Considering eqn. 44, the expression for the retention volume becomes

$$V_{R,cc} = V_{\mu/vNA} + S \left[ \frac{d\Psi_{A/vNA}}{d\varphi_{\mu,A}} + \alpha \left( \frac{d\Psi_{A/vNA}}{d\varphi_{\mu,A}} + \frac{\varphi_{\mu,A} - \varphi_{\mu,B}}{\varphi_{\mu,A}\varphi_{\mu,B}} \cdot \Psi_{A/vNA} \right) \right] \varphi_{\mu,A}^0 \quad (94)$$

If the mixture is ideal (*i.e.*, the molar volume is a linear function of  $x_{\mu,A}$ ), the coefficient  $\alpha$  is zero (see eqn. 92), and eqn. 94 takes the simple form given in Table I.

## SYMBOLS

### *Symbols*

$c$  (mol l<sup>-1</sup>), concentration;  $d$  (g cm<sup>-3</sup>) =  $1/\tilde{v}$ , density;  $\Gamma$  (mol m<sup>-2</sup>), surface concentration;  $\varphi$  (—) =  $p\tilde{v}/\tilde{v}_{\mu}$  =  $xv/v_{\mu}$ , volume fraction;  $k$  (—) =  $c_s/c_{\mu}$ , partition coefficient;  $\chi$  (mol m<sup>-2</sup> or g m<sup>-2</sup> or ml m<sup>-2</sup>), peak propagation resistivity;  $L$  (cm), column length;  $m$  (g), mass of eluent or solute;  $m$  (—), number of components in a fluid mixture;  $M$  (g mol<sup>-1</sup>), molar mass;  $n$  (mol), number of moles of eluent or solute;  $N$  (—): number of components in the liquid mixture (in particular, eluent);  $v$  (ml mol<sup>-1</sup> or ml g<sup>-1</sup> or no units), constant in eqn. 45;  $p$  (—), mass fraction;  $\bar{P}$  (bar), mean pressure;  $\Pi$  (g m<sup>-2</sup>), surface concentration;  $\Psi$  (ml m<sup>-2</sup>  $\approx$   $\mu$ m), surface concentration;  $S$  (m<sup>2</sup>), surface area of a solid;  $t$  (min), time;  $T$  (°K), temperature;  $v$  (ml mol<sup>-1</sup>), (partial) molar volume;  $\bar{v}$  (ml g<sup>-1</sup>), (partial) specific volume;  $V$  (ml), volume;  $\dot{V}$  (ml min<sup>-1</sup>), flow-rate;  $V_R$  (ml), retention volume;  $V_N$  (ml), net retention volume;  $V_S$  ( $\mu$ l m<sup>-2</sup>), surface specific retention volume;  $V_g$  (ml g<sup>-1</sup>), specific retention volume;  $w$  (g), mass referring to the stationary phase;  $x$  (—), molar fraction;  $z$  (cm), distance in the column.

### *Subscripts*

A, ..., J, ..., N, components of the eluent; cc, peak due to concentration per-

turbation; *su*, solute; *i*, either J, cc or *su*; *c*, column;  $\beta$ , bulk of the liquid; CX, convention X (GLC, model for gas-liquid chromatography or one of the conventions JNA, *nNA*, *mNA* and *vNA*);  $\kappa$ , column capacity (total of a component in the column transported by the mobile phase);  $\mu$ , mobile phase;  $\sigma$ , [two meanings], (i) of the stationary phase and (ii) material adsorbed or absorbed in the stationary phase; S, unit surface area; tot, sum over all components present;  $\tau$ , total amount in (or of) a mixture before adsorption.

### Superscripts

0, before the beginning of the chromatographic process; (id), ideal dilution.

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### REFERENCES

- 1 D. de Vault, *J. Amer. Chem. Soc.*, 62 (1940) 1583.
- 2 G. G. Baylé and A. Klinkenberg, *Rec. Trav. Chim. Pays-Bas*, 73 (1954) 1037.
- 3 P. C. Mangelsdorf, Jr., *Anal. Chem.*, 38 (1966) 1540.
- 4 F. Helfferich and G. Klein, in J. C. Giddings and R. A. Keller (Editors), *Multicomponent Chromatography — Theory of Interference*, Marcel Dekker, New York, 1970.
- 5 G. Schay, *Ber. Bunsenges. Phys. Chem.*, 77 (1973) 184.
- 6 R. M. McCormick and B. L. Karger, *J. Chromatogr.*, 199 (1980) 259.
- 7 R. M. McCormick and B. L. Karger, *Anal. Chem.*, 52 (1980) 2249.
- 8 J. H. Knox and R. Kaliszan, to be published, but cited in J. H. Knox, R. Kaliszan and G. J. Kennedy, *Faraday Symposium No. 15, Brighton, 1980*, Royal Society of Chemistry, London, 1980, p. 113.
- 9 J. H. Knox and E. sz. Kováts, discussion contribution, *Faraday Symposium No. 15, Brighton, 1980*, Royal Society of Chemistry, London, 1980, p. 177.
- 10 C. L. de Ligny, discussion contribution, *Faraday Symposium No. 15, Brighton, 1980*, Royal Society of Chemistry, London, 1980, p. 171.
- 11 E. H. Slaats, W. Markovski, J. Fekete and H. Poppe, *J. Chromatogr.*, 207 (1981) 299.
- 12 E. H. Slaats, *Doctoral Thesis*, University of Amsterdam, 1980.
- 13 M. Jaronec, B. Oscik-Mendyk, A. Dabrowski and H. Kolodziejczyk, *J. Liquid Chromatogr.*, 4 (1981) 277.
- 14 G. E. Berendsen, P. J. Schoenmakers, L. de Galan, G. Vigh, Z. Varga-Puhony and J. Inczédy, *J. Liquid Chromatogr.*, 3 (1980) 1669.
- 15 P. Fini, F. Brusa and L. Chiesa, *J. Chromatogr.*, 210 (1981) 326.
- 16 P. Valentin and G. Guiochon, *J. Chromatogr. Sci.*, 14 (1976) 56 and 132.
- 17 J. F. K. Huber and R. G. Gerritse, *J. Chromatogr.*, 58 (1971) 137.
- 18 A. A. Zhukhovitskii, *Gaz-Khromatogr. Akad. Nauk. S.S.S.R. Tr. Vtoroi. Vses. Konf., Moskow*, (1962) 5; *C.A.*, 62 (1965) 5868. See also in A. Goldup (Editor), *Gas Chromatography 1964*, Institute of Petroleum, London, 1965, p. 161.
- 19 A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, 35 (1941) 1358.
- 20 K. Karch, I. Sebastian, I. Halász and H. Engelhardt, *J. Chromatogr.*, 122 (1976) 171.
- 21 A. W. J. de Jong, J. C. Kraak, H. Poppe and F. Nooitgedacht, *J. Chromatogr.*, 193 (1980) 181.
- 22 J. L. M. van de Venne, *Doctoral Thesis*, University of Eindhoven, Eindhoven, 1979.
- 23 E. H. Slaats, J. C. Kraak, W. J. T. Brugman and H. Poppe, *J. Chromatogr.*, 149 (1978) 255.
- 24 G. Körösi and E. sz. Kováts, *Coll. Surf.*, 2 (1981) 315.
- 25 Ngoc Le Ha, *Doctoral Thesis*, École Polytechnique Fédérale de Lausanne, Lausanne, in preparation.