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## COMPARISON BETWEEN THE CONDITIONS FOR SOLUTE FOCUSING BY THE STATIC AND DYNAMIC SOLVENT EFFECTS UNDER IDEAL CONDITIONS

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### SUMMARY

In capillary gas chromatography static and dynamic solvent effect inlets provide quantitatively precise methods of sample introduction of solutes which fulfill the conditions for solute focussing. Equations are derived for the conditions for focussing on static and dynamic films. In the case of a static film a solute will be focussed if the sum of its partition coefficient between the gas phase and the film and the phase ratio are greater than the partition coefficient of the solvent. On dynamic solvent films solutes whose partition coefficients are larger than those of the solvent are focussed.

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### INTRODUCTION

The static and dynamic solvent effects are manifestations of the peculiar chromatographic properties of mechanically stable, evaporating solvent films<sup>1-4</sup>. Inlets which employ the static or dynamic solvent effects offer uniquely precise methods of sample introduction for capillary gas chromatographic analysis<sup>5,6</sup>. Dynamic solvent effect sampling has been successfully applied to a variety of problems in semiochemistry<sup>7-11</sup>.

Here we present comparative models of the behaviour of static and dynamic sample films under ideal conditions, that is, in the absence of band spreading. In the interest of a clearer comparison between the two systems the treatment of the static solvent effect differs somewhat from that presented by Deans<sup>1</sup> and Pretorius *et al.*<sup>2</sup>.

### THE STATIC SOLVENT EFFECT

Consider a tube with a porous layer on its inside wall, in which a pure liquid is held by capillary attraction as a mechanically stable film. Along the axis of the tube is an open channel down which flows a stream of gas at a velocity sufficiently low that the shape of the liquid film is not altered by shear forces. The liquid will evaporate into, and be carried away by, the stream of gas at a rate governed by the liquid's vapour pressure and the volume flow-rate of the gas. Under conditions of ideal gas behaviour

the mass rate of removal of the solvent vapour is given by (symbols are defined at the end of the text)

$$E_{om} = \frac{P_v V_g m_o}{RT} \quad (1)$$

The mass rate at which liquid evaporates from the film must, obviously, be the same as the mass rate of removal of the vapour. The evaporation rate in terms of liquid volume is then

$$E_{ov} = \frac{E_{om}}{\rho_o} \quad (2)$$

$$= \frac{P_v V_g m_o}{RT \rho_o} \quad (3)$$

Provided that equilibrium between the gas and liquid phases is quickly established the gas will become saturated with vapour after passing over only a short length of the film. Evaporation will then effectively be confined to the upstream edge of the film. Because the film is held in place by the capillarity of the porous layer in which it lies, evaporation at the upstream edge removes liquid from that area alone. As a result of this removal the position of the film's edge moves downstream. The film therefore becomes shorter, but does not move as a whole with respect to the tube wall.

The rate at which the upstream edge moves at a given evaporation rate is determined by the volume of liquid held in unit length of the film, which is given by

$$A_o = \frac{Q_o}{l_f} \quad (4)$$

$A_o$  is simply the cross sectional area of the liquid annulus, and the rate of downstream movement of the position of the upstream edge of the film is the volume evaporation rate divided by this area:

$$U_o = \frac{E_{ov}}{A_o} \quad (5)$$

$$= \frac{P_v V_g m_o}{RT \rho_o A_o} \quad (6)$$

Now consider the behaviour of a volatile solute dissolved in the liquid film. Being volatile it will partition between the gas and the liquid and will consequently be carried chromatographically downstream at a velocity determined, in the absence of lagging<sup>12</sup>, by its partition ratio and the gas linear velocity:

$$v_x = \frac{U_g}{k_x + 1} \quad (7)$$

If, at the upstream edge of the film the solute is moving downstream faster than the position of the film's upstream edge *i.e.* if

$$v_x > U_o \quad (8)$$

the solute concentration at the upstream edge of the film will fall as the solute is moved forward and ultimately stripped from the film by the gas. If, on the other hand, the solute moves downstream more slowly than the film's edge *i.e.* if

$$v_x < U_o \quad (9)$$

at the upstream edge of the film the solvent is being removed from the solution by evaporation faster than the solute is being removed by chromatographic migration. The solute's concentration consequently rises. These solutes are focussed by the static solvent effect.

If the gas contains volatiles before it encounters the liquid film the vapours will impinge on, and dissolve in, the upstream edge of the film. They will then behave in the same way as solutes originally in the film.

Inequality 9 can be rewritten from eqn. 6 as

$$v_x < \frac{P_v V_g m_o}{RT \rho_o A_o} \quad (10)$$

The linear flow-rate of the gas phase is its volume flow-rate per unit area of the gas channel's cross section:

$$U_g = \frac{V_g}{A_g} \quad (11)$$

Eqn. 10 then becomes

$$v_x < \frac{P_v U_g A_g m_o}{RT \rho_o A_o} \quad (12)$$

The area of the gas channel and that of the liquid annulus determine the phase ratio:

$$\beta = \frac{A_g}{A_o} \quad (13)$$

Substituting in eqn. 12 then gives

$$v_x < \frac{P_v U_g m_o \beta}{RT \rho_o} \quad (14)$$

Substituting from eqn. 7 in eqn. 14, and rearranging:

$$(k_x + 1) > \frac{RT\rho_o}{P_v m_o \beta} \quad (15)$$

Consider now the partitioning of the solvent between the liquid and gas phases. For dilute solutions the concentration of solvent in the liquid phase is the solvent density. The concentration in the gas phase is the mass rate of solvent evaporation into the volume of gas sweeping the film in unit time (eqn. 1):

$$k_o = \frac{RT\rho_o}{P_v m_o \beta} \quad (16)$$

Eqn. 15 can now be rewritten:

$$(k_x + 1) > k_o \quad (17)$$

$$k_x = \frac{K_x}{\beta} \quad (18)$$

$$k_o = \frac{K_o}{\beta} \quad (19)$$

The condition for solute focussing by the static solvent effect then becomes

$$(K_x + \beta) > K_o \quad (20)$$

#### CONSEQUENCES OF SOLUTE FOCUSING BY THE STATIC SOLVENT EFFECT

As the upstream edge of the liquid film moves downstream solutes for which the condition for solvent effect focussing is met accumulate in a short band at the upstream edge of the film. In the ideal case the length of the band of concentrated solutes is small compared to the length of the film, and the solute focussing mechanism continues to operate until nearly all the film has evaporated. At this stage the length of the film has become the same as that of the concentrated band so that the solutes are no longer chromatographically retarded by a film of liquid lying downstream of them. The last traces of the liquid film therefore consist of a concentrated solution of the solutes occupying a short region of the porous layer at the position previously occupied by the downstream end of the liquid film. It is the high concentration and small volume of the solution which makes possible its efficient transfer to a capillary column, and it is in this respect that static solvent effect focussing is useful as a sampling technique for large, dilute, liquid specimens.

#### THE DYNAMIC SOLVENT EFFECT

In the case of the dynamic solvent effect the downstream end of the film is in

contact with a source of the liquid it consists of. Now when gas is passed over the film, liquid removed by evaporation from its upstream edge is replaced by liquid drawn by capillary attraction from the liquid source. Thus there is a continuous bulk movement of liquid towards the evaporation zone, which retains its position until the source of liquid is removed. Solutes are carried towards the evaporation zone by this bulk movement of liquid, and in the opposite direction by the gas. Solutes whose net upstream velocity is higher than their net downstream velocity accumulate in the evaporation zone<sup>4</sup>.

Consider a tube with a porous layer on its inside wall and an open channel along its axis. If the tube is dipped into a liquid which wets the porous layer the liquid will rise into it (passage of liquid into the axial channel is ignored for present purposes).

The height to which the liquid will rise against gravity is given by<sup>13</sup>

$$h = \frac{2\gamma}{\rho_0 g r_h} \quad (21)$$

If the porous layer can be approximated by a random packing of solid, spherical particles<sup>14</sup>:

$$r_h = \frac{\varepsilon}{S_p(1 - \varepsilon)} \quad (22)$$

$$S_p = \frac{6(1 - \varepsilon)}{d_p} \quad (23)$$

and from eqns. 21, 22 and 23:

$$h = \frac{12\gamma(1 - \varepsilon)^2}{\rho_0 g \varepsilon d_p} \quad (24)$$

For *n*-hexane, the most commonly used solvent,  $\gamma = 20 \text{ dynes cm}^{-1}$ ,  $\rho = 0.7 \text{ g cm}^{-3}$  and for randomly packed spheres  $\varepsilon = 0.35$ , and if the mean size of the particles is 0.1 mm:  $h = 376 \text{ mm}$ . This is six to seven times as high as the liquid film rises when the dynamic solvent effect is used for sampling. Consequently the effects of hydrostatic pressure on the behaviour of the film can be neglected in the following model.

When there is no pressure gradient, as here, the velocity with which a liquid enters a pore due to capillarity is given by<sup>13</sup>

$$U_{pp} = \frac{r_h \gamma}{4\eta L} \quad (25)$$

The speed with which a liquid front is drawn into a porous bed is reduced by the tortuosity of the channels in which it flows:

$$U_{pb} = \frac{U_{pp}}{\tau} = \frac{r_h \gamma}{4\eta L \tau} \quad (26)$$

The volume rate at which the liquid flows into the porous layer depends on the cross sectional area of the liquid annulus:

$$V_{pb} = \frac{r_h \gamma A_o}{4\eta L \tau} \quad (27)$$

The volume of liquid held in the porous layer depends on the length of wetted bed and the liquid annulus cross sectional area:

$$Q_o = l_f A_o \quad (28)$$

When gas is passed down the axial channel the liquid which has risen into the bed will evaporate into the gas. As in the case of the static film (eqn. 3) evaporation will be confined to the upstream edge of the film and its rate will be given by

$$E_{ov} = \frac{m_o V_g P_v}{RT \rho_o} \quad (29)$$

If the rate of evaporation is greater than the rate at which liquid flows into the porous layer there will be a decrease with time in the volume of liquid in the layer and from eqn. 28 the length of the film will decrease ( $A_o$  is fixed by the geometry of the porous layer).

Since

$$l_f = \frac{L}{\tau} \quad (30)$$

and from eqn. 27 the volume of liquid entering the bed is inversely dependent on the length of the pores through which the liquid has to permeate, the shortening of the film allows a faster flow-rate into the porous layer. As the film shortens a point is reached at which

$$V_{pb} = E_{ov} \quad (31)$$

and no further change in film volume, film length or liquid flow-rate occurs. The upstream edge of the liquid film will now hold a fixed position within the porous layer, and liquid is supplied to it by capillarity at a rate given by eqn. 27, and removed from it by evaporation at a rate given by eqn. 29.

In this equilibrium condition

$$V_{pb} = \frac{m_o V_g P_v}{RT \rho_o} \quad (32)$$

The average linear velocity of the upward movement of the liquid is related to the volume flow of liquid by eqns. 26 and 27:

$$U_{pb} = \frac{m_o V_g P_v}{RT \rho_o A_o} \quad (33)$$

so that, as is intuitively obvious, the liquid in a dynamic solvent film flows upstream with the same linear velocity as that with which the upstream edge of the equivalent static film moves downstream.

Under equilibrium conditions solutes are moved chromatographically away from the evaporation zone by the gas, and towards it by the liquid flow.

The rate of downstream movement is given by

$$v_{xd} = \frac{U_g}{(k_x + 1)} \quad (34)$$

and the rate of upstream movement by

$$v_{xu} = \frac{U_{pb}}{\frac{1}{k_x} + 1} \quad (35)$$

Solutes for which

$$v_{xd} > v_{xu} \quad (36)$$

experience a net downstream movement and are stripped from the liquid film (compare eqn. 8).

Solutes for which

$$v_{xd} < v_{xu} \quad (37)$$

experience a net upstream movement towards the evaporation zone, where they accumulate. This is the condition for solute focussing by the dynamic solvent effect (compare eqn. 9).

From eqns. 34 and 35 inequality 37 can be rewritten as

$$\frac{U_g}{k_x + 1} < \frac{U_{pb}}{\frac{1}{k_x} + 1} \quad (38)$$

$$\frac{U_{pb}}{\frac{1}{k_x} + 1} = \frac{U_{pb} \cdot k_x}{k_x + 1} \quad (39)$$

Inequality eqn. 38 then becomes

$$U_g < (U_{pb} \cdot k_x) \quad (40)$$

$$k_x > \frac{U_g}{U_{pb}} \quad (41)$$

now:

$$U_g = \frac{V_g}{A_g} \quad (42)$$

and so from eqn. 33:

$$k_x > \frac{V_g}{(m_o V_g P_v A_g)/(RT \rho_o A_o)} \quad (43)$$

$$k_x > \frac{1}{(m_o P_v \beta)/(RT \rho_o)} \quad (44)$$

$$k_x > \frac{RT \rho_o}{m_o P_v \beta} \quad (45)$$

As in the case of the static film (eqn. 16),

$$k_o = \frac{\rho_o RT}{P_v m_o \beta} \quad (46)$$

so that eqn. 45 can be rewritten:

$$k_x > k_o \quad (47)$$

from which it follows that solutes for which

$$K_x > K_o \quad (48)$$

will be focussed by the dynamic solvent effect. Thus the condition for solute focussing by the dynamic solvent effect is somewhat more stringent than that for focussing by the static solvent effect.

#### SYMBOLS

$A_g$	cross sectional area of gas channel
$A_o$	cross sectional area of liquid annulus
$d_p$	mean particle diameter in a porous material
$E_{om}$	mass rate of solvent evaporation
$E_{ov}$	volume rate of solvent evaporation
$g$	acceleration due to gravity
$h$	height of a liquid column



$k_o$	partition ratio of solvent between itself and the gas
$k_x$	partition ratio of solute between liquid and gas
$K_o$	partition coefficient of solvent between itself and the gas
$K_x$	partition coefficient of solute between liquid and gas
$l_f$	length of liquid film
$L$	length of a pore
$m_o$	molecular weight of solvent
$M_o$	mass of solvent
$P_v$	partial pressure of a vapour
$Q_o$	volume of liquid
$r_h$	hydraulic radius
$R$	universal gas constant
$S_p$	specific surface area of a porous solid
$T$	temperature
$U_f$	velocity of upstream edge of film
$U_g$	linear velocity of gas
$U_{pb}$	linear velocity with which a liquid permeates a porous solid
$U_{pp}$	linear velocity with which a liquid permeates a pore
$v_x$	chromatographic velocity of solute plug (static film)
$v_{xd}$	chromatographic downstream velocity of a solute plug (dynamic film)
$v_{xu}$	chromatographic upstream velocity of a solute plug (dynamic film)
$V_g$	volumw flow-rate of gas
$V_{pb}$	volume rate at which liquid flows into a porous solid
$\beta$	phase ratio
$\eta$	viscosity
$\varepsilon$	porosity of a porous solid
$\tau$	tortuosity of the pores in a porous solid
$\gamma$	surface tension of a liquid
$\rho_o$	density of solvent

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