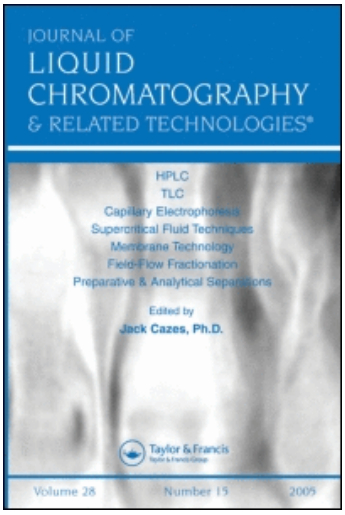

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A Kinetic and Quantitative Approach to Peak Splitting Phenomena When Using 2-Propanol as Modifier in Adsorption HPLC

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A KINETIC AND QUANTITATIVE APPROACH TO PEAK SPLITTING PHENOMENA WHEN USING 2-PROPANOL AS MODIFIER IN ADSORPTION HPLC

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ABSTRACT

When using 2-propanol as a modifier in adsorption chromatography, a "satellite" peak is observed if a shight excess of a polar chlorinated hydrocarbon, such as CH_2Cl_2, is injected.
This satellite peak whose appearance is related to the presence of 2-propanol, has been identified as a part of the CH_2Cl_2 injected.
The satellite peak behaves chromatographically mainly as a normal solute peak and its area is proportional to both the amount of CH_2Cl_2 injected and the concentration of 2-propanol in the mobile phase and on the other hand inversely related to the flow-rate and the concentration of CH_2Cl_2 in the mobile phase.
A physico-chemical model is proposed based on the perturbance of the dynamic equilibrium when the sample enters the column. The model is compatible with the experimental results and explains the origin of the satellite peak as well as its chromatographic behaviour. It also allows a better understanding of the role of a modifier related to its adsorption-desorption process.

INTRODUCTION

The addition of a modifier, such as 2-propanol, to the mobile phase up to a concentration of 1 or 2% v/v, is of common use in adsorption HPLC. As mentioned in recent papers (1,3) there is still need for experimental and theoretical evidence to get a good understanding of the modifiying mechanism. On the other hand a modifier often causes peakshape distortion (2,3).

This paper deals with the kinetic and quantitative approach of a phenomenon, which to our knowledge has not been reported, namely the splitting up into two peaks of a single product injection. When injecting methylenechloride, chloroform or 1,2-dichloroethane as a solute and making use of 2-propanol/iso-octane (0.5/99.5 % v/v) as mobile phase on a Si-or CN-modified Si-column, a second "satellite" peak is observed in addition to the solute peak. This second peak, characterised by a convex front tailing and a compressed rear, has been identified as a part of the injected solute.
Although it is also connected with the use of a modifier, in this case 2-propanol, this phenomenon of peak splitting is quite different from the "vacancy" peaks or displaced solvent peaks described in literature (4,5,6,7,8,9). A complex adsorption-isotherm and zone compression or peak shapening effects (10,11,12) could explain the convex shape of the peak, but not the peak splitting phenomenon. The origin of the "satellite" peak can neither be explained by the conventional dynamic approach nor by the thermodynamic "near by" equilibrium, usually described in relation to chromatographic processes (11,12,13,14).

We approach this peak splitting phenomenon by a dynamic model that also takes account of the quantitative aspect of the formation of the "satellite" peak. This model can also contribute to a better understanding of the fundamental behaviour of a modifier as it shows the Snyder-Soczewinski displacement model (15,16) to be more appropriate than the the Scott-Kucera solution interaction model (17,18,19) when low concentrations of high solvents in the mobile phase are involved.

EXPERIMENTAL

The chromatographic set-up consists of a Waters Assoc. M-6000 pump, a Waters Assoc. U6K injector equipped with a 2 ml sol-

vent loop and a Waters Assoc. R401 differential refractometer with external thermostatisation. The temperature of the flow-through cells is kept at 2°C below ambient to prevent degasing of the solvent in the cells. The RI detector output is connected to a Hewlett Packard 3370B integrator and a BD9 Kipp & Zonen recorder.

Columns used are : Lichrosorb Merck Si 100 (5μ), 250 mm x 4 mm
Chrompack Sil-60D-10CN (10 μ), nitrile, 250 mm x 4.6 mm
Waters Assoc. μPorasil, 10μ , 350 mm x 3.9 mm
Waters Assoc. μCN, Nitrile on μPorasil 10μ , 350 mm x 3,9 mm.

Home distilled CH_2Cl_2 (Solvay) and i-octane (Phillips Petroleum) are used for the major part of the experiments. The average water content of the CH_2Cl_2, as determined by GC analysis, is about 0.009%.

The other solvents such as 2-propanol, $CHCl_3$, 1,2-dichloroethane, CCl_4, and the CH_2Cl_2 used as control standard are HPLC or analytical reagent grade.

The sample injection volume varied from 1-100 μl, but 15 μl is used as a standardized amount for undiluted solvent samples. The standard flow-rate is 2 ml/min.

The mobile phase and the eluted peaks are collected at the detector outlet.

The gas chromatographic analysis of these samples is carried out on a Varian 3760 gas chromatograph equipped with a 6" x 1/8" column of 0.2% Carbowax 1500 on 60/80 Carbopack C (Supelco, Inc.) coupled to a FID detector. The column oven is isothermally heated at 70° C. After four chromatographic runs, the iso-octane present in the sample, is flushed off by heating the column at 125° C during 10 minutes.

RESULTS AND DISCUSSION

Experimental results

- When injecting 1 μl or more of CH_2Cl_2, 1,2-dichloroethane, $CHCl_3$ the peak splitting phenomenon characterized by the presence of a "satellite" peak is observed as long as 2-propanol is present in the mobile phase. A detailed chromatogram (fig.1) shows the expected solute peak "S" and the "satellite" peak "P", the latter preceeded by a negative peak, obtained when injecting 15 μl of CH_2Cl_2 into a

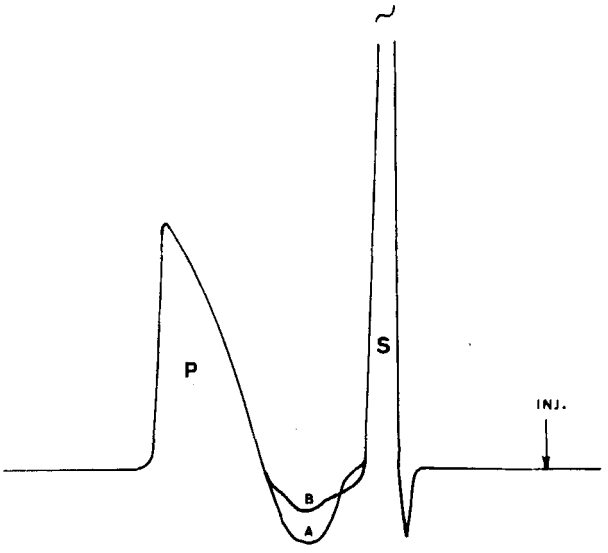

Fig. 1 : S : CH_2Cl_2 solvent peak; P : satellite peak; A : 15 µ CH_2Cl_2 injected; B : 150 µl of CH_2Cl_2 1/10 diluted in mobile phase.

mobile phase stream consisting of 2 propanol/iso-octane (0,5/99,5 % v/v) using a CN modified silica column. On the other hand no splitting effect is obtained when injecting CCl_4, 2-propanol or iso-octane.

The satellite peak has been identified by G.C. analysis (see experimental) as a portion of the injected chlorinated hydrocarbon, the remainder constituting the principal solute peak. The negative peak preceeding the satellite peak has been identified as a displaced 2-propanol peak.

When injecting a mixture of CH_2Cl_2 and $CHCl_3$ or 1,2-dichloroethane, both products are found in a common "satellite" peak.

If a more polar solvent, such as CH_2Cl_2, is present in the mobile phase the convex assymetry of the "satellite" peak decreases toghether with the backtailing of the negative 2-propanol peak.

One on the other hand when the same amount of the polar chlorinated hydrocarbon, diluted in the eluent is injected, a decrease of the negative peak is observed.

When plotting $1/t_{R'}$, $t_{R'}$ representing the corrected retention time of the "satellite" peak, as a function of the volumetric flow-rate $\bar{v}$, a linear relationship is obtained showing a slope equal to $1/V_{R'}$, $V_{R'}$ being the corrected retention volume.

As to the quantitative aspect of the satellite peak "P", it is experimentally proven that :

- The area P of the satellite peak increases linearly with the amount of solute injected up to 30 µl for a 4.6 mm x 250 mm column (fig.2) and can vary from 0-20% of the solute peak, depending on the experimental conditions described in the following section.

The area is directly proportional to the concentration of 2-propanol in the mobile phase Cp, (fig.3)

$$P = \alpha . Cp$$

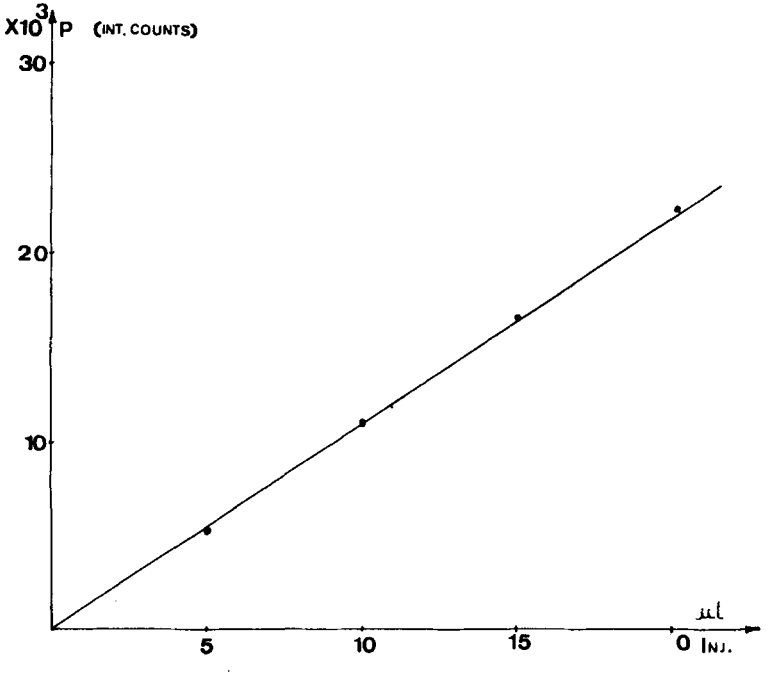

Fig. 2 : Area P of the satellite peak (integrator counts) as a function of the amount of CH_2Cl_2 injected; CN-column.

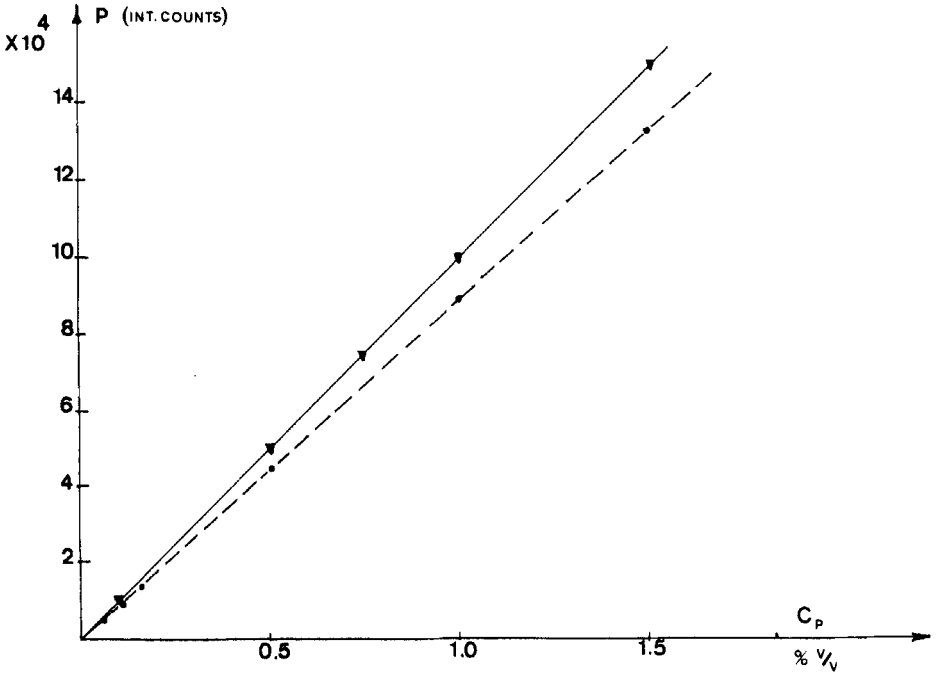

Fig. 3 : Area P (integrator counts) as a function of C_p; x C_p in % v/v in CH_2Cl_2/i-octane (30/70 v/v); --o-- CN column:—▼— Si column.

- When CH_2Cl_2 is already present in the mobile phase, the relation between P and the CH_2Cl_2 concentration in the eluent C_m, represented in fig. 4, can be written as :

$$1/P = a + bC_m$$

- P is inversely related to $\bar{v}$ as shown in fig. 5. Above a flow-rate of 4 ml/min the satellite peak begins to collapse with the solute peak and dissapears completely at higher flow-rates.

Discussion

Adsorption chromatography is governed by an adsorption-desorption process, which can generally be described by a "Langmuir-isotherm"-like expression (10, 12, 14, 22). Analogous to the Frenkel relation (23),

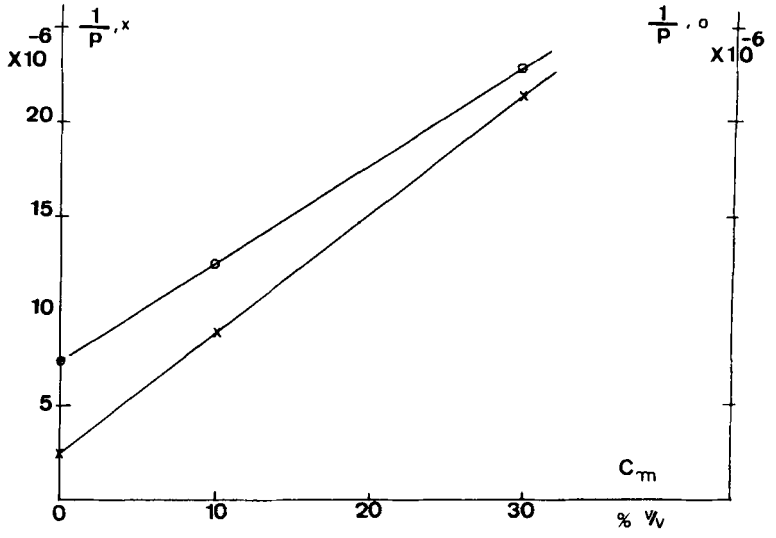

Fig. 4 : 1/P (integrator counts) as a function of C_m; CN-column.
Left ordinate : -X- 0,5 % 2-propanol in x CH_2Cl_2/100-x i-octane.
Right ordinate : --[●]-- 0,1 % 2-propanol in x CH_2Cl_2/100-x i-octane.

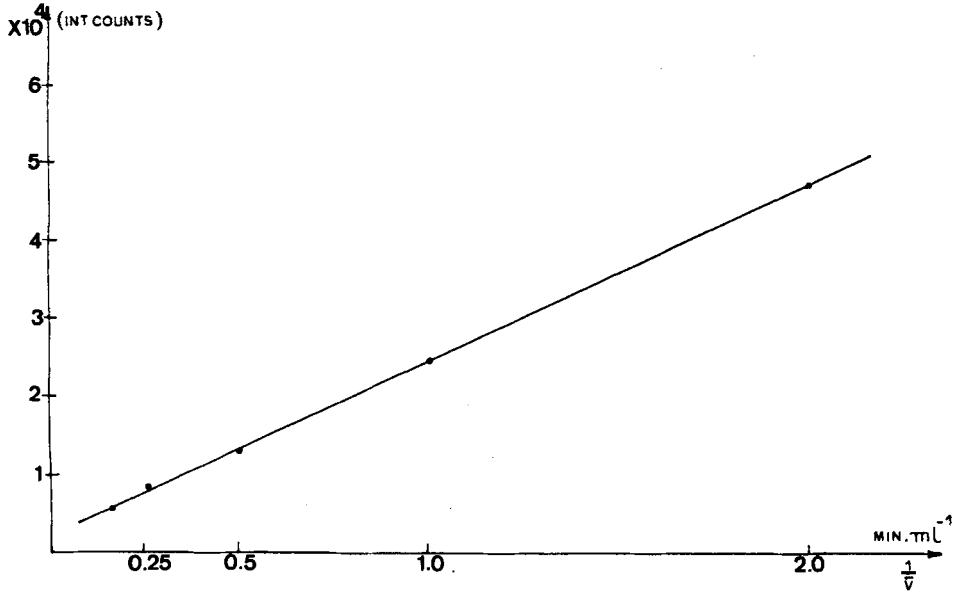

Fig. 5 : Area P (integrator counts) as a function of $1/\bar{v}$; 0.15 % 2-propanol in CH_2Cl_2/i-octane (30/70 v/v); CN column.

the residence or adsorption time τ of solute or solvent molecules on the active sites of the adsorbent can be defined as

$$\tau = \tau_0 \, e^{\Delta G^t_{S,M} / RT} \qquad (3)$$

Here $\Delta G^t_{S,M}$ stands for the free energy of transfer, related to the difference of the interaction forces between solute -adsorbent and solute-mobile phase; τ_0 is the proportionality constant (23).

It is assumed that the modifying interaction of 2-propanol, or any other modifier, can be described as a dynamic equilibrium and that the efficiency of occupying the more active sites is determined by its adsorption time τ on those sites and will depend on $\Delta G^t_{S,M}$, thus on the polarity of the mobile phase.

Polarity is used here in the general sense, namely the ability to engage in hydrogen bonding or dipole-dipole interactions.

The residence time τ of 2-propanol on the sites of lower activity will be smaller, resulting in an increase of the accessibility of those sites to other molecules.

The latter type of sites can be called "available" sites.

The splitting of a solute peak, resulting in the formation of a "satellite" peak can neither be described by a "near equilibrium" model (12,13), nor by a non linear isotherm (6,10,11).

Our interpretation of the origin of peak splitting, due to the presence of a modifier such as 2-propanol in adsorption HPLC, is related to the disturbance of the dynamic equilibrium of the modifier-adsorbent interaction, starting as the injected solute enters the column. The appearance of peak splitting will also depend on the relative strength of the interaction forces the injected solute and the modifier present in the mobile phase with the adsorbent.

We present a first approach based on a simple dynamic model, omitting complex mathematical derivations and neglecting peak broadening diffusion phenomena.

For the sake of simplicity, but still obeying realistic conditions, the mobile phase is supposed only to consist of the modifier 2-propanol in iso-octane. As solute a small amount of CH_2Cl_2 is injected. We further assume that the iso-octane molecules cannot compete with the CH_2Cl_2 and 2-propanol molecules for adsorption sites and that

the sites occupied by 2-propanol are of higher activity, corresponding to its role of modifier.

Let'sconsider a small volume element V_i at the column inlet. When the amount of CH_2Cl_2 injected enters this element, the concentration in the mobile phase of CH_2Cl_2, $c_{M,m}$, is high while that of 2-propanol $c_{M,p}$, decreases considerabely.

At that moment $\frac{c_{S,p}}{c_{M,p}} \gg k_p$, kp being the partition coefficient at equilibrium. This causes the 2-propanol molecules to desorb from the more active sites at a rate given by

$$r_{d,p} = k_{d,p} \cdot c^{eq}_{S,p} \qquad (4)$$

$k_{d,p}$: the desorption rate constant of 2-propanol from the more active sites in contact with the CH_2Cl_2 plug.

$c^{eq}_{S,p}$: the concentration of 2-propanol in the absorbed state on the more active sites at equilibrium conditions before injection of the CH_2Cl_2 sample.

The injected CH_2Cl_2 entered in V_i is now involved into a twofold adsorption-desorption process.

1° The first being a fast dynamic interaction with the "available" sites of lower activity. This allows the mass balance of CH_2Cl_2 in V_i at that moment to be written as :

$$\frac{dc_m}{dt} = - \bar{\mu} \frac{dc_m}{dz} + k_{d,m} c_{S,m} - k_{a,m} c_m (c^{\circ}_{S,m} - c_{S,m}) \qquad (5)$$

$\bar{\mu}$: the mean linear flow rate; z : distance from the column inlet

$c_{S,m}$: the actual concentration of CH_2Cl_2 on the adsorbent

$c^{\circ}_{S,m}$: the concentration if all the "available" sites are occupied

c_m : the concentration of CH_2Cl_2 in the mobile phase

$k_{a,m}$ and $k_{d,m}$: the adsorption and desorption rate constants.

2° On the other hand the CH_2Cl_2 molecules also interact with the more active sites as they become available by the desorption of 2-propanol. As the amount of this kind of sites becoming available per unit of time, depends on the desorption rate $r_{d,p}$ of 2-propanol,

the adsorption rate $r'_{a,m}$ of CH_2Cl_2 will only depend on $r_{d,p}$ as long as its actual concentration, governed by eq.5, is sufficiently high. As the activity of these sites is higher than that of the "available" ones, the adsorption time τ of CH_2Cl_2 on these sites will also be larger (eq.3) than on the "available" sites. The desorbed 2-propanol, on its path through V_i, will be involved in an adsorption-desorption process different from the equilibrium state and will thus behave as a "displaced solvent" peak.

3° When the total amount of the CH_2Cl_2 injected has penetrated into the column, fresh eluent mixture enters V_i. Now $C_{M,p}$ increases rapidly in V_i and the 2-propanol molecules are involved in a fast adsorption process, taking the place of the CH_2Cl_2 molecules "adsorbed" on the sites of higher activity during 2°.
At the end of the column this results in a CH_2Cl_2 solute peak S (fast equilibrium, Cfr. 1°) and a retarded CH_2Cl_2 satellite peak "p" (slow exchange, cfr. 2° and 3°).

The area of the satellite peak P is directly related to the amount of CH_2Cl_2 involved in the adsorption process described in 2°. This amount is proportional to the adsorption rate $r'_{a,m}$ of CH_2Cl_2 on the sites of higher activity and the time θ during which the adsorption occurs.
P can be estimated by

$$P \sim r'_{a,m} \cdot \theta \qquad (6)$$

The desorption rate of 2-propanol is described by equotion 4 wherein $C^{eq}_{S,p}$ may be substituted by its value from the Langmuir-isotherm, as it corresponds to the adsorbed concentration of 2-propanol at equilibrium, before the injection of the CH_2Cl_2 sample :

$$C^{eq}_{S,p} = \frac{C_p \cdot C^{\circ}_{S,p} \cdot K^{eq}_p}{1 + K^{eq}_p \cdot C_p} \qquad (7)$$

K^{eq}_p is the adsorption equilibrium constant for 2-propanol
For Cp sufficiently small, this results in

$$r_{d,p} = k_{d,p} \cdot K^{eq}_p \cdot C^{\circ}_{S,p} \cdot Cp \qquad (8)$$

The assumption made about Cp in order to obtain equation (8) seems to be realistic as the maximal analytical concentration used is 1,5% v/v or 0.016 g/g.

The adsorption rate $r'_{a,m}$ of CH_2Cl_2 on the more active sites is mainly determined by the desorption rate of 2-propanol from those sites allowing equation (8) to be written as

$$r_{a,m} \sim r_{d,p} = k_{d,p} \cdot K_p^{eq} \cdot C^{\circ}_{S,p} \cdot C_p \qquad (9)$$

Substituting eq.9 in eq.6 gives

$$P \sim k_{d,p} \cdot K_p^{eq} \cdot C^{\circ}_{S,p} \cdot C_p \cdot \theta \sim \mathcal{K} \cdot \theta \cdot Cp \qquad (9')$$

We now consider θ' as the residence time of a small plug of CH_2Cl_2 passing through V_i .

As long as the residence time τ of 2-propanol on the more active sites is smaller than θ', the CH_2Cl_2 molecules can absorb on those sites and $\theta' = \theta$, θ is the time during which adsorption occurs and can be written as :

$$\theta = \theta' = \frac{V_i}{\bar{v}} \qquad (10)$$

$\bar{v}$: the volumetric flow rate

Substituting equation (10) in (9') gives :

$$P \sim \mathcal{K} \cdot V_i \cdot \frac{1}{\bar{v}} \cdot Cp \qquad (11)$$

Equation (11) clearly corresponds to the experimental results described above and shown in the Figures 3 and 5. On the other hand, if CH_2Cl_2 is present already in the mobile phase, before the injection of the sample, the adsorption time τ of 2-propanol decreases and the CH_2Cl_2 molecules now compete in the equilibrium adsorption-desorption process for their share of higher activity-sites.

According to Saunders (24) the resulting isotherm equation for 2-propanol, if Cp is small, can be written as :

$$C^{eq}_{S,p} = \frac{K_p^{eq} \cdot Cp}{1 + K_m^{eq} \cdot C_m^{eq}} \qquad (12)$$

with K_m^{eq} : the adsorption equilibrium constant for CH_2Cl_2 already present in the mobile phase

C_m^{eq} : the analytical concentration of CH_2Cl_2 in the mobile phase.

Substituting equation (12) in (4) and assuming that

$$r'_{a,m} \sim r_{d,p} \; ; \quad \text{gives}$$

$$r'_{a,m} = k_{d,p} \frac{K_p^{eq} \cdot Cp}{1 + K_m^{eq} \cdot C_m^{eq}} \qquad (13)$$

and

$$P \sim \frac{V_i}{\bar{v}} \cdot k_{d,p} \cdot \frac{K_p \cdot Cp}{1 + K_m^{eq} \; C_m^{eq}} \qquad (14)$$

with $\alpha = \frac{V_i \cdot k_{d,p}}{\bar{v}}$ and $b = \frac{\bar{v} \cdot K_m^{eq}}{V_i \cdot k_{d,p} \cdot Cp}$

equation (14) can be rearranged as

$$\frac{1}{P} = \frac{1}{\alpha Cp} + b \; C_m^{eq} \qquad (15)$$

It is shown that equation (15) is compatible with all experimental results. (see Figs. 3 and 5)

Our dynamic model accounts for both the interaction of the solute molecules with the adsorbent and the solvent. Our interpretation of the contribution of the adsorption time and $\Delta G^t_{S,M}$ (equation 3) to the fundamental role of the modifier can explain the Scott-Kucera interpretation of solvent interaction at higher concentrations of polar solvent in the eluent. At high "modifier" concentrations, in the range to 10-90%, as described in the experiments of Scott and Kucera (18), the polar solvent does not act as "modifier" anymore. In the model of these authors two mechanisms are mixed up, namely a selective occupation of sites of higher activity and the solute-modifier interaction at high modifier concentrations when all the sites of the adsorbent are saturated.

Our model is consistent with the remark of Snyder and Poppe (1) that solutes or solvents with lower polarity than the modifier can compete with the modifier molecules.

On the other hand our results prove that anommalous peak-shape effects and even peak splitting do occur when slow desorption kinetics of the modifier are involved and this in total agreement with the theory of the Snyder-Soczewinski displacement model (1,15,16) assuming a dynamic equilibrium for the modifier and a monolayer adsorption as proposed by Snyder, Poppe et al (1,15, 16,20,21,22).

CONCLUSION

It may be concluded that the experimental results do confirm the theoretical relations derived from the physico-chemical model.
The moderating role of 2-propanol, and of any modifier, is related to a dynamic adsorption-desorption process, whereby the adsorption time τ is a function of the interaction forces in both the mobile and solid phase.

When this equilibrium process is perturbated, due to the fact that the interaction forces and the related kinetic parameters of a solute are of the same order of magnitude as those of the modifier, a process resulting in peak splitting can occur. This will result in a more or less separated "satellite" peak, depending on the concentration and the interaction strength of the modifier and on the polarity of the mobile phase.

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