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EXPERIMENTAL STUDY OF SYSTEM PEAKS AND ELUTION PROFILES FOR LARGE CONCENTRATION BANDS IN THE CASE OF A BINARY ELUENT CONTAINING A STRONGLY SORBED ADDITIVE

SADRODDIN GOLSHAN-SHIRAZI and GEORGES GUIOCHON*

**Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 (U.S.A.) and Division of Analytical Chemistry, Oak Ridge National Laboratory, Oak Ridge, TN (U.S.A.)*

SUMMARY

Band profiles of high-concentration samples of single compounds eluted from a silica column by a binary mobile phase were recorded under various sets of experimental conditions. The mobile phase was a dilute solution (0.02–2%, v/v) of light alkanols in dichloromethane or *n*-hexane. When the concentration of the strong solvent increases at a constant sample size, or the sample size increases at a constant strong solvent concentration, the elution profile, which is first of the type associated with a Langmuir adsorption isotherm with a sharp front and a slanted tail, changes the direction of its asymmetry and becomes similar in shape to the profiles associated with an anti-Langmuir isotherm, with a slanted front and a sharp tail. The shape of the profiles in the transition range is unusual and appears similar to the composite of two or three different bands. Finally, at large sample sizes and high strong solvent concentrations, the profile develops a hump on its front, which eventually may turn into a second peak.

These experimental profiles are in excellent qualitative agreement with those predicted by theory and described in the accompanying paper. Their variations with the experimental parameters follow the trends predicted in that study. The competition between the molecules of the strong solvent (or modifier) and those of the samples is entirely responsible for these profiles.

INTRODUCTION

In a previous paper[1], we discussed from a theoretical standpoint the profiles of high and very high concentration bands eluted by a binary solvent mixture. The aim of this work was to compare these theoretical results with experimental results and to show how a number of phenomena that have remained unexplained so far can be accounted for and possibly used.

When a sample is injected into a chromatographic column swept by a mobile phase that is not a single solvent but a mixture, several peaks are observed, some of which are negative. These peaks, which are usually called system peaks, have been known for a long time[2]. They have been used for isotherm determinations[3], as a method for the UV detection of compounds without a chromophore[4,5] and for the

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direct determination of equilibrium constants[6]. An excellent review of the origin, formation and importance of system peaks has been published by Levin and Grushka[7].

System peaks are due to the perturbation of the equilibrium between the mobile phase and the stationary phase as the sample penetrates the column and its molecules compete with those in the mobile phase which interact with the stationary phase. The net result of this competition, if the sample is retained at all, is in the expulsion from the stationary phase of a small amount of the adsorbed components of the mobile phase. This amount corresponds to the amount of sample adsorbed on the stationary phase at equilibrium, under the experimental conditions selected. The expelled amounts of these components travel along the column at their own speed, as a function of the extent of their adsorption. When the sample is eluted, the adsorbed solvent components of the mobile phase must replenish the stationary phase and thus equilibrium between the two phases is reached again. Accordingly, the elution of the sample band is accompanied by a negative solvent band. Depending on (i) the sample size, (ii) the adsorption strength ratio of the strong solvent and the sample and (iii) the ratio of the response factors of the detector for the sample and the strong solvent, the corresponding peak may be positive, negative or almost negligible in size.

Previous work on system peaks[2–8] dealt essentially with the quasi-linear aspect. Chromatography is certainly not linear in the present instance, as it involves two characteristic properties of non-linear chromatography: (i) the amount of strong solvent adsorbed at equilibrium is not proportional to its concentration in the mobile phase; the strong solvent adsorption isotherm is usually not linear in the concentration range used in the mobile phase; and (ii) the retention time of a small sample pulse depends on the concentration of the strong solvent, which is why the strong solvent (or additive) is used in the first place. However, it is possible to consider the problem of the elution of a small sample plug as a problem in linear chromatography, because a function can be replaced by its two-term expansion around any of its values, in order to calculate the effect of a very small change in the variable. The linear treatment of system peaks under analytical conditions is therefore justified, as they constitute small perturbations. However, it should not be forgotten that the isotherms involved are the mixed, competitive isotherms, expressing quantitatively how the amount of compound A_s (strong solvent, mobile phase additive or sample) which is sorbed by the stationary phase at equilibrium depends on the concentration of all the components present in the mobile phase.

The purpose of this work was different. We are interested in studying the problems involved in preparative liquid chromatography and the answers can only be obtained by considering the entire problem, which involves the solution of the system of non-linear mass balance equations describing the behavior of the components of the mobile phase and the sample. This requires a knowledge of the mixed, competitive equilibrium isotherms of all the species involved or, alternately, of the kinetics of mass transfers between phases of all these species. For most implementations of chromatography, the kinetics of mass transfer are fast enough to justify assuming the two phases to be near equilibrium at all times[9]. We can therefore use the semi-ideal model[10]. The prediction of the profiles of high-concentration bands eluted by a binary mobile phase is therefore a two-compound problem, requiring a system of two mass balance equations (one for the sample and one for the additive or strong solvent). If the

mobile phase is a ternary solvent or contains two additives, the prediction of the profile of a high-concentration band of a single compound becomes a three-component problem, and the prediction of the profiles for a two-component sample with a ternary mobile phase becomes a four-component problem.

In the accompanying theoretical paper[1] we considered the elution profile of a high-concentration band eluted by a binary mobile phase and the influence of various experimental parameters. Here we compare the theoretical results with those obtained experimentally.

EXPERIMENTAL

A Hewlett-Packard (Palo Alto, CA, U.S.A.) Model 1090 liquid chromatograph, equipped with a diode-array detector and a data station, was used for most of the experiments. Also employed for experiments involving the study of the solvent peaks was a Waters Assoc. (Milford, MA, U.S.A.) Model 410 differential refractive index detector, connected to the HP datastation through an HP dual-channel interface. A 25 cm × 1/4 in. O.D. × 4.6 mm I.D. stainless-steel column packed with 15–25-μm silica particles was used.

The mobile phases were derived either from dichloromethane, modified with various amounts of one of the strong organic solvents methanol, ethanol, 2-propanol and *tert.*-butanol, or from *n*-hexane, modified by mixing with different concentrations of 2-propanol. The compositions are reported in the figure captions.

The solutes investigated were 2-phenylethanol, 3-phenyl-1-propanol and 2-phenyl-1-propanol from Fluka (Ronkonkoma, NY, U.S.A.) and acetophenone from Fisher Scientific (Pittsburgh, PA, U.S.A.). The sample size was varied between 0.02 and 25 μl.

RESULTS AND DISCUSSION

Twenty years ago it was suggested that strongly polar organic solvents, such as alcohols, could be used as organic modifiers in weakly polar or non-polar mobile phases, such as *n*-hexane or dichloromethane, in order to control the activity of the silica[11]. Kirkland[12] published a detailed study on the influence of water and various alcohols as organic solvent modifiers in normal-phase liquid chromatography. Very small concentrations of these additives were required; typically, concentrations between 0.05 and 0.3% of methanol, ethanol or 2-propanol were recommended[12].

Kirkland[12] reported very unusual band shapes in some instances. He noted a change in the elution profile with increasing alcohol content, the direction of asymmetry of the peak changing from tailing to fronting, with an intermediate stage where the band "appears as the superimposition of two different chromatographic bands". Punčochářova *et al.*[13] noted similar phenomena in the elution profiles of bands of cyclohexanol and cyclohexanone on silica with various binary mobile phases.

As these experiments showed the importance of the effect of alkanols as organic modifiers, we decided to investigate the behavior of system peaks generated by the injection in this kind of mobile phase of large or very large sample sizes, and also the profiles of the sample peaks.

Experimental study of the solvent peak

Our theoretical results[1] showed that the elution of a high-concentration pulse of sample is accompanied by a solvent peak, which occurs as a result of the coupling between the adsorption of the solvent and the sample on the stationary phase. The use of a refractive index detector is necessary to record the solvent band, as the UV absorption of alkanols is negligibly small at accessible wavelengths.

We used dichloromethane containing 1% of 2-propanol as the mobile phase. Fig. 1 shows a chromatogram obtained with 2-phenylethanol as the sample. The refractive indices of dichloromethane, 2-propanol and 2-phenylethanol are 1.4244, 1.3772 and 1.532, respectively. Although the response factors are not directly proportional to the differences between the refractive indices of the solutes and that of the weak solvent, we may expect to see a negative peak when the concentration of the strong solvent increases in the weak solvent and a positive peak when the concentration of the sample increases[14]. This inversion of the response sign must be kept in mind when looking at the chromatograms and trying to understand what is happening in the column.

Fig. 1 shows the chromatograms for four pulses of 2-phenylethanol (1, 2, 5 and 10 μl). The inset is a simulated chromatogram corresponding to a strongly sorbed organic modifier (ratio of the origin slopes of the adsorption isotherms of the strong solvent and the sample from their dilute solution in the pure weak solvent equal to 2). It permits an easy understanding of what is happening here.

The simulated elution profile (Fig. 1, inset) exhibits one sample band and two bands for the strong solvent, a positive peak eluted before the sample band and a negative peak eluted at the same time as the sample band[1]. The area of these system peaks increases with increasing sample size. At large sample sizes, the positions of the first solvent band and of the sample peak depend not only on the adsorption strength

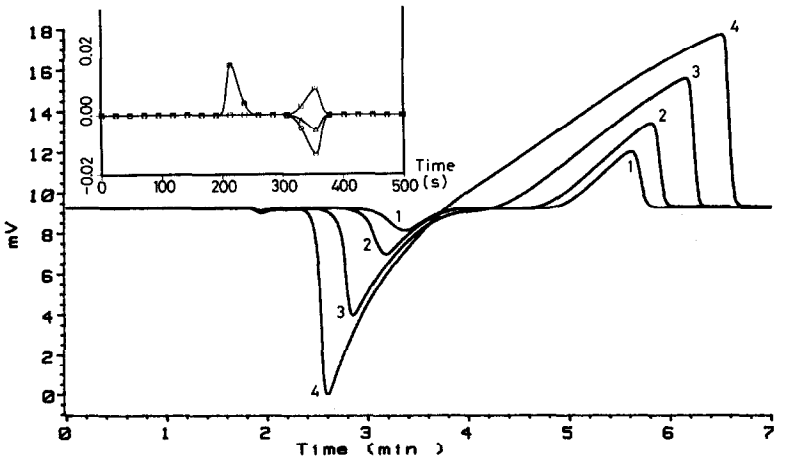


Fig. 1. Elution chromatograms of pulses of 2-phenylethanol of increasing sample size. Refractive index detector. Comparison with theoretical predictions. Column, 25 cm × 4.6 mm I.D.; mobile phase, dichloromethane containing 1% 2-propanol (*i.e.*, 0.17 *M*); stationary phase, silica, 15–25-μm particles; flow-rate 2 ml/min. Sample size: 1, 1 μl; 2, 2 μl; 3, 5 μl; 4, 10 μl. Inset. Simulated chromatogram with competitive Langmuir isotherms for the strong solvent and the sample. Langmuir coefficients: $a_a = 40$; $a_s = 80$; $b_a = 8$; $b_s = 16$ (see ref. 1). Concentration of strong solvent, 0.17 *M*; sample size, 1 μl.

of the strong solvent (*i.e.*, the slope at the origin of its adsorption isotherm between the pure weak solvent and the stationary phase), but also on the sample size (see Figs. 1 and 2). The position of the sample peak (at least at zero sample size) also depends on the strength of adsorption of this compound. With increasing sample size, the two bands of the pure solvent and the sample approach closer to each other and eventually interfere with each other[1].

The experimental results (see Fig. 1, curves 1–4) confirm these predictions. As the response factor is negative for the strong solvent and positive for the sample, the first peak (strong solvent) is recorded as a negative signal, while the effects of the strong solvent band add to those of the sample band in the recording of the second, mixed band (the second solvent band is negative in concentration, *i.e.*, positive in signal with the refractive index detector). The area of the first system peak increases with increasing sample size. The first system peak and the sample band approach closer to each other, and the resolution between these two bands becomes lower than unity for a sample size larger than 5 μl (see Fig. 1, curves 3 and 4).

The same phenomenon is observed in Fig. 2, which shows the chromatograms recorded for the elution of samples of increasing size (1, 5 and 10 μl) of 3-phenyl-1-propanol. The resolution between the system peak and the sample band is larger at small sample sizes, because 3-phenyl-1-propanol is more strongly adsorbed than 2-phenylethanol, and thus these bands begin to interfere with each other markedly only for the largest sample (see Fig. 2).

The strength of adsorption of the three phenylalkanols used in this work decreases in the order 3-phenyl-1-propanol, 2-phenylethanol and 2-phenyl-1-propanol. Fig. 3 shows the chromatograms obtained for the same amounts of these three compounds (5 μl) when injected separately. The retention time of the maximum of the system peak (first solvent peak) increases with increasing sample adsorption, whereas the retention of the sample band increases in order of increasing strength of adsorption (order of increasing retention times: 2-phenyl-1-propanol < 2-phenylethanol < 3-

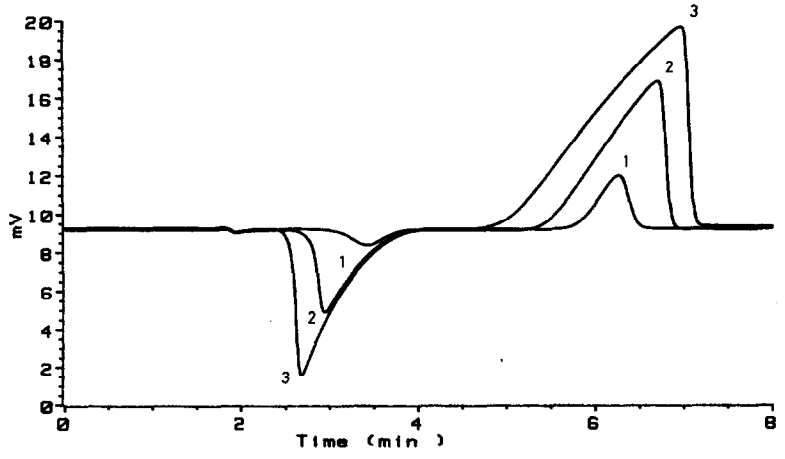


Fig. 2. Elution chromatograms of pulses of 3-phenyl-1-propanol of increasing sample size. Refractive index detector. Experimental conditions as in Fig. 1. Sample size: 1, 1 μl; 2, 5 μl; 3, 10 μl.

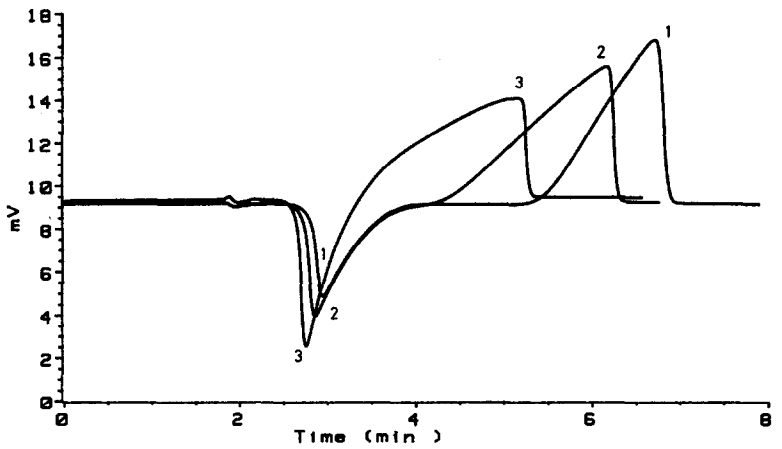


Fig 3. Elution chromatograms of pulses of different single compounds of same sample size (5 μl). Refractive index detector. Experimental conditions as in Fig. 1. 1, 3-Phenyl-1-propanol; 2, 2-phenylethanol; 3, 2-phenyl-1-propanol.

phenyl-1-propanol). The degree of resolution between the strong solvent and solute bands improves in the same order.

These experimental results confirm the predictions of our theoretical model[1].

Experimental study of the sample peak. Influence of the nature of the modifier

The remainder of this study was performed with a diode-array UV detector, and therefore there is no contribution of the changes in the strong solvent concentration and of the system peaks in the recorded chromatograms. The only effect of the strong solvent results from its competition with the sample for the adsorption sites at the surface of the silica.

Figs. 4–7 show the elution chromatograms of pulses of various amounts of 3-phenyl-1-propanol on silica when other alcohols are used as modifiers: 1% *tert.*-butanol (Fig. 4), 1% 2-propanol (Fig. 5), 1% ethanol (Fig. 6) and 0.5% methanol (Fig. 7). Comparison between Figs. 1 and 5 shows that there is little difference between the shapes of the true sample profiles (Fig. 5) and those of the profiles of the second band eluted from the column (Fig. 1).

In all instances, the elution profiles show leading peaks, with a sharp shock layer on their rear, and a retention time of the band maximum that increases with increasing sample size. This behavior is usually associated with an anti-Langmuir isotherm. This conclusion would be correct with a pure mobile phase but it is obviously not true here. The equilibrium isotherms may not be properly represented by true competitive Langmuir isotherms; this theoretical model is too crude to account quantitatively for the behavior of most real systems. Nevertheless, the curvature of the isotherms is negative. The behavior of the system when the sample size, the organic modifier concentration or its nature is changed is not consistent with an anti-Langmuir type of isotherm. For example, when the sample size is increased for a system with a true anti-Langmuir isotherm, all the bands start at the same time[15]. This is not the case in Figs. 4–7. Further, within some range of strong solvent concentrations (see Figs. 11

and 14), we observe band profiles that are typical of those traditionally associated with a Langmuir isotherm (or at least typical of an isotherm with a negative curvature).

The polarity of the alcohol and hence the strength of its adsorption on silica increase with decreasing length of its alkyl chain. The retention times of the bands, especially the limiting retention time (retention time of the smallest sample size that gives an almost symmetrical peak), decrease in the order *tert.*-butanol, 2-propanol, ethanol (see Figs. 4–7). The band shapes observed with methanol (see Fig. 7) are very unusual, but very similar to those predicted by the theoretical study (see ref. 1, Figs. 4 and 9).

Figs. 8 and 9 show chromtograms obtained with a weaker solvent (*n*-hexane instead of dichloromethane), modified with 1% of 2-propanol. Two compounds were used as pure samples, 3-phenyl-1-propanol and the much less polar acetophenone.

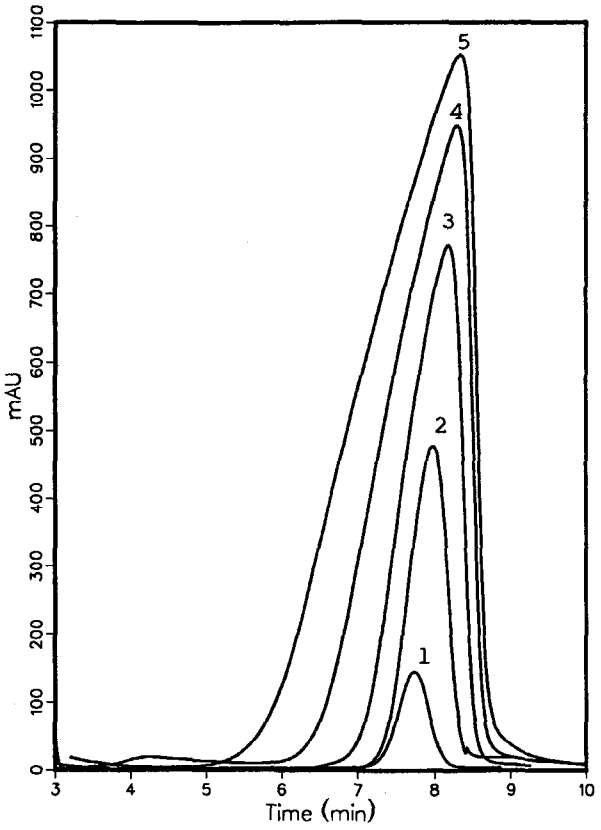
Because *n*-hexane is a weaker, less polar solvent than dichloromethane, the saturation capacity of the column is larger. Accordingly, the effect of the adsorption of the strong solvent on the band profile of the sample is smaller, as shown in Fig. 8 (*cf.*, Fig. 6). The elution profile of 3-phenyl-1-propanol is now similar to that observed with a pure mobile phase for a compound with a weakly curved Langmuir isotherm.

On the other hand, acetophenone is much less polar than 3-phenyl-1-propanol, less strongly adsorbed and less retained (*cf.*, Figs. 8 and 9). The strength of adsorption of the strong solvent is much higher than that of the sample and the elution profiles become very unusual, as shown in Fig. 9. At first, when the sample size increases from zero, the band profile evolves as in the case of an anti-Langmuir isotherm, but then (see curve 4 in Fig. 9) the front part of the band also becomes very steep, the profile becomes a smooth rectangle and eventually a sharp peak arises at low retention times. This corresponds precisely to the situation predicted by the theoretical study when the strong solvent is much more strongly retained than the sample (see ref. 1, Fig. 9).

Experimental study of the sample peak. Influence of the concentration of the modifier

Fig. 10 shows the elution bands obtained for the chromatography of increasing amounts of acetophenone with a binary mobile phase consisting of 2-propanol–*n*-hexane (2:98). Compared with Fig. 9 the change in elution profile is less pronounced, but it is as striking. The bands remain narrower and there is no trend towards a change in the direction of asymmetry, but now the large bands have two maxima. Common sense would lead one to think that either the sample is impure or there is something wrong with the entrance packing section of the column (it is not unusual that the packing at the column inlet becomes inhomogeneous or even that a hole forms, resulting in band profiles similar to those of chromatograms 5 and 6 in Fig. 10). The phenomenon is also reminiscent of that observed by Kirkland[12].

A systematic investigation of the influence of the concentration of the strong solvent on the elution band profile was carried out, using dichloromethane as the weak solvent and 2-propanol as the strong solvent. The concentration of 2-propanol was increased from 0.1 to 0.2 and 1%. Samples of various sizes of 2-phenylethanol and 3-phenyl-1-propanol were injected. The chromatograms are shown in Figs. 11–17. The theoretical study[1] showed that at low concentrations of strong solvent the behavior of the band profile is "normal", *i.e.*, it is similar to what would be expected when overloading a column in the case of a Langmuir isotherm. The band becomes increasingly asymmetric, with a very sharp front (shock layer) and a smooth tail



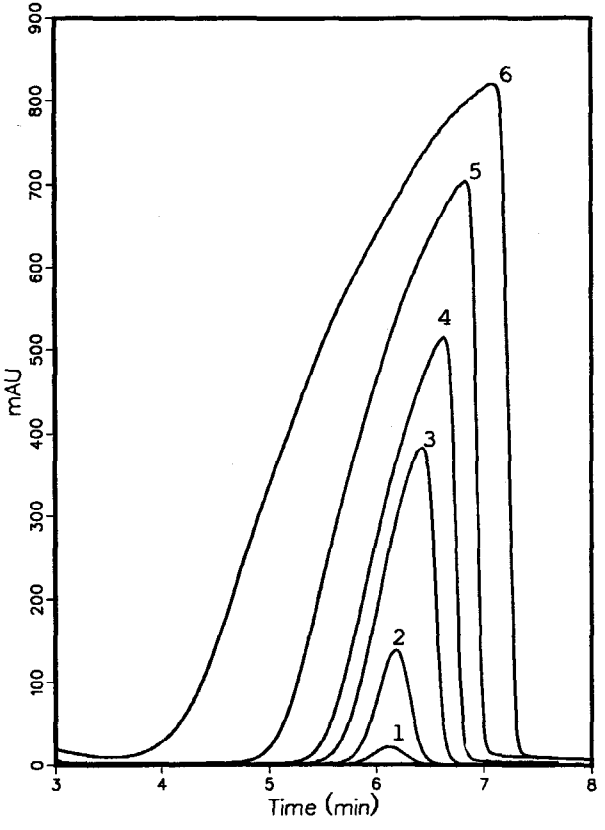


Fig. 4. Elution chromatograms of pulses of 3-phenyl-1-propanol of increasing sample size. UV detector at 270 nm (no response for the solvent). Column, 25 cm × 4.6 mm I.D.; mobile phase, dichloromethane containing 1% *tert.*-butanol; stationary phase, silica, 15–25-μm particles; flow-rate, 2 ml/min. 1, 0.4 μl; 2, 2 μl; 3, 6 μl; 4, 15 μl; 5, 25 μl.

Fig. 5. Elution chromatograms of pulses of 3-phenyl-1-propanol of increasing sample size. UV detector (no response for the solvent). Experimental conditions as in Fig. 4, except 1% 2-propanol as strong solvent. 1, 0.08 μl; 2, 0.4 μl; 3, 2 μl; 4, 4 μl; 5, 8 μl; 6, 20 μl.

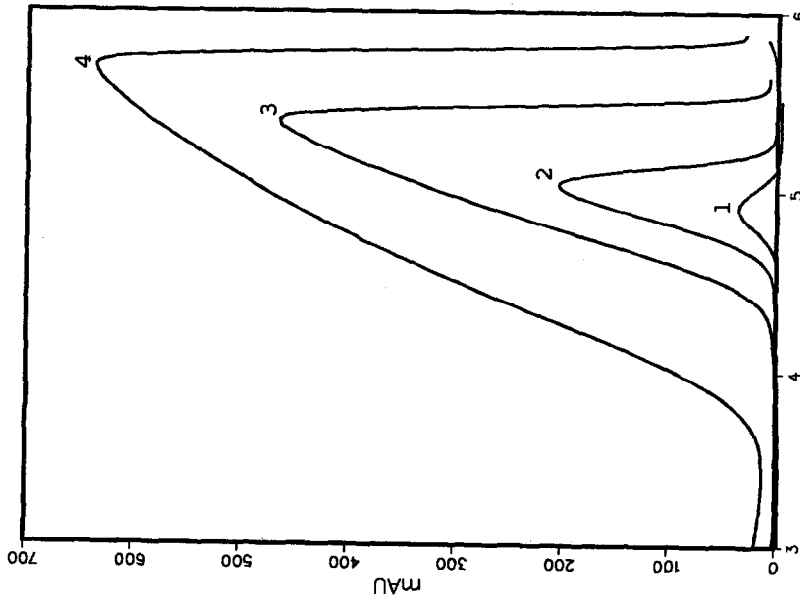


Fig. 6. Elution chromatograms of pulses of 3-phenyl-1-propanol of increasing sample size. UV detector (no response for the solvent). Experimental conditions as in Fig. 4, except 1% ethanol as strong solvent. 1, 0.08 μl; 2, 0.4 μl; 3, 2 μl; 4, 6 μl.

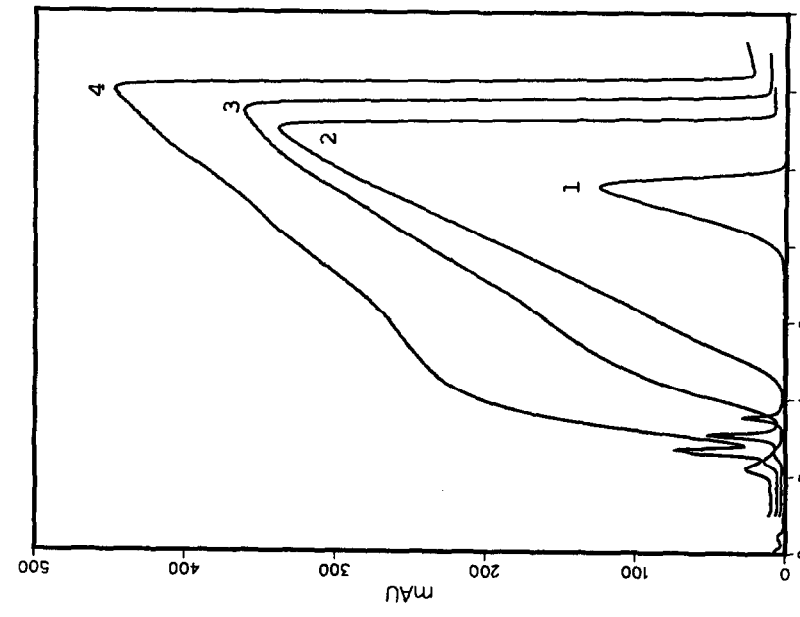


Fig. 7. Elution chromatograms of pulses of 3-phenyl-1-propanol of increasing sample size. UV detector (no response for the solvent). Experimental conditions as in Fig. 4, except 0.5% methanol as strong solvent. 1, 0.4 μl; 2, 4 μl; 3, 6 μl; 4, 10 μl.

Fig. 8. Elution chromatograms of pulses of 3-phenyl-1-propanol of increasing sample size. UV detector (no response for the solvent). Experimental conditions as in Fig. 4, except 1% 2-propanol as strong solvent and *n*-hexane as weak solvent. Flow-rate, 3 ml/min. 1, 1 μl; 2, 5 μl; 3, 10 μl; 4, 15 μl; 5, 25 μl.

Fig. 9. Elution chromatograms of pulses acetophenone of increasing sample size. UV detector at 320 nm (no response for the solvent). Experimental conditions as in Fig. 4, except 1% 2-propanol as strong solvent and *n*-hexane as weak solvent. Flow-rate, 1 ml/min. 1, 0.02 μl; 2, 1 μl; 3, 2 μl; 4, 5 μl; 5, 10 μl; 6, 15 μl; 7, 25 μl.

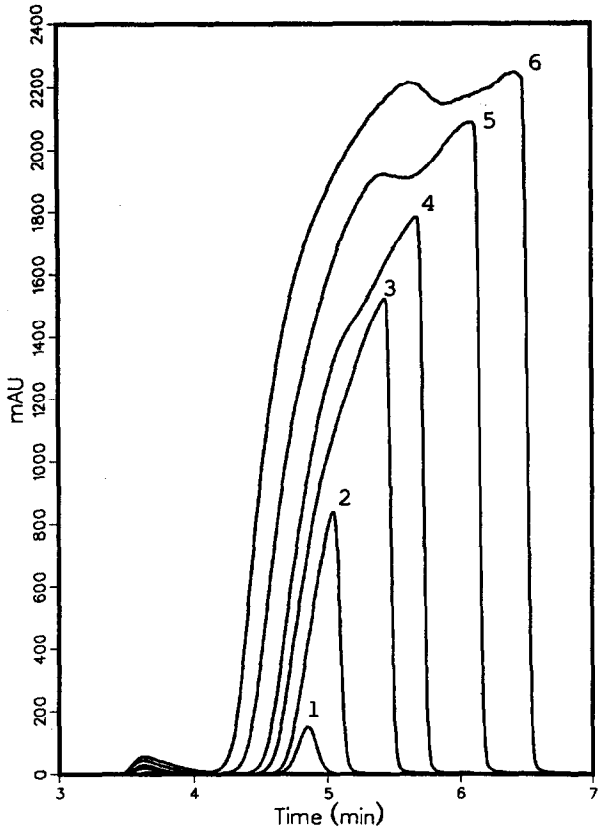
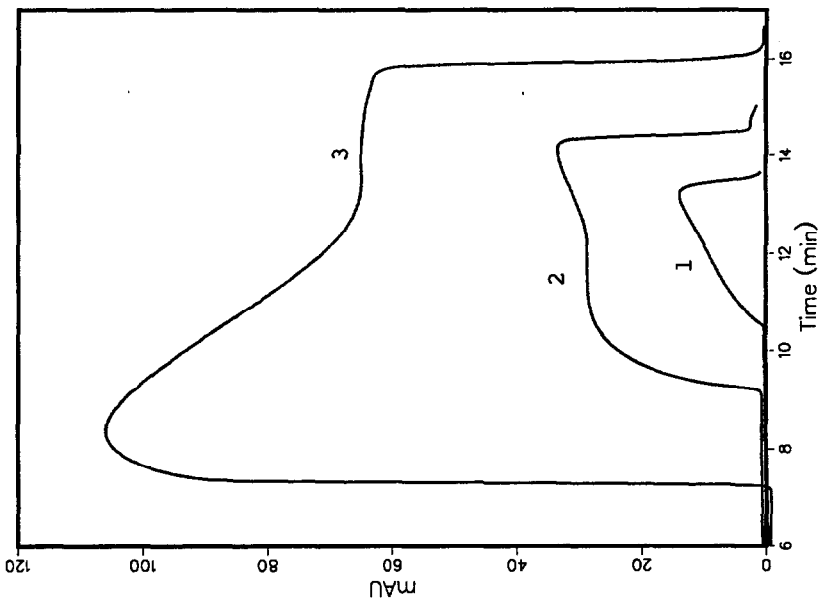


Fig. 10. Elution chromatograms of pulses of acetophenone of increasing sample size. UV detector (no response for the solvent). Experimental conditions as in Fig. 9, except 2% 2-propanol as strong solvent. 1, 0.02 μl; 2, 1 μl; 3, 3 μl; 4, 5 μl; 5, 10μl; 6, 15 μl.

extending until the retention time of the sample at infinite dilution. When the concentration of the strong solvent is high, the reverse behavior is predicted by the theory of chromatography. The bands are leading, with a smooth (diffuse) front and a sharp rear part. There is a narrow range of strong solvent concentrations in which the band profile reverses itself and the bands assume extremely odd shapes[1].

The experimental results confirm these predictions. Fig. 11 shows the profiles obtained with a concentration of 0.1% 2-propanol, with samples of 0.2, 1 and 10 μl of 2-phenylethanol. The profiles are typical of those obtained for a Langmuir isotherm. Fig. 12 shows the chromatograms obtained for sample sizes of 0.2, 1 and 5 μl of the same compound when the mobile phase contains 0.2% 2-propanol. The band profile has completely changed and is extremely unusual. However, it is very similar to the profiles calculated by our simulation program (see ref. 1, Figs. 6 and 12). Fig. 13 shows the chromatograms recorded with a mobile phase containing 1% 2-propanol with samples of the same compound of 0.2, 1, 5, 10 and 15 μl. The profile asymmetry has changed direction compared with the peaks in Fig. 11, and the bands are similar to (but



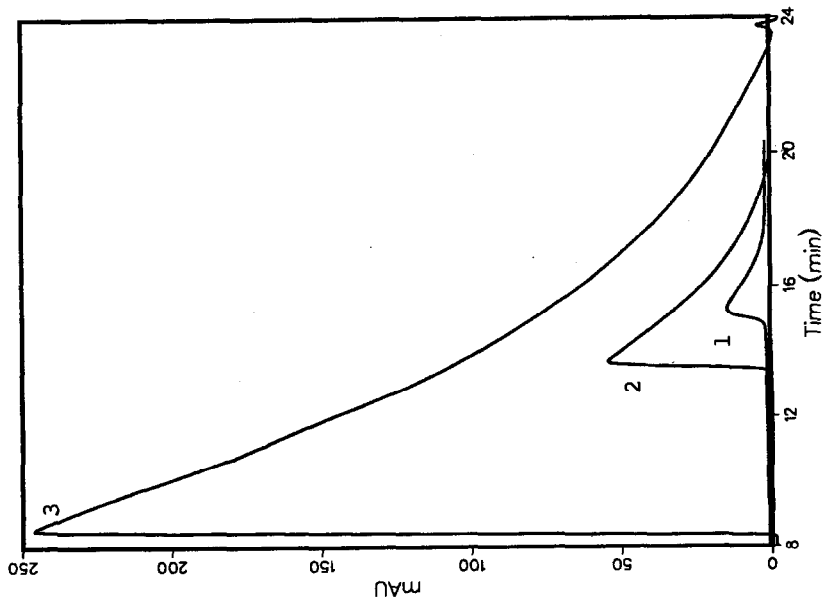


Fig. 11. Elution chromatograms of pulses of 2-phenylethanol of increasing sample size. UV detector (no response for the solvent). Experimental conditions as in Fig. 4, except 0.1% 2-propanol as strong solvent. 1, 0.2 μl; 2, 1 μl; 3, 10 μl.

Fig. 12. Elution chromatograms of pulses of 2-phenylethanol of increasing sample size. UV detector (no response for the solvent). Experimental conditions as in Fig. 11, except 0.2% 2-propanol as strong solvent. 1, 0.2 μl; 2, 1 μl; 3, 5 μl.

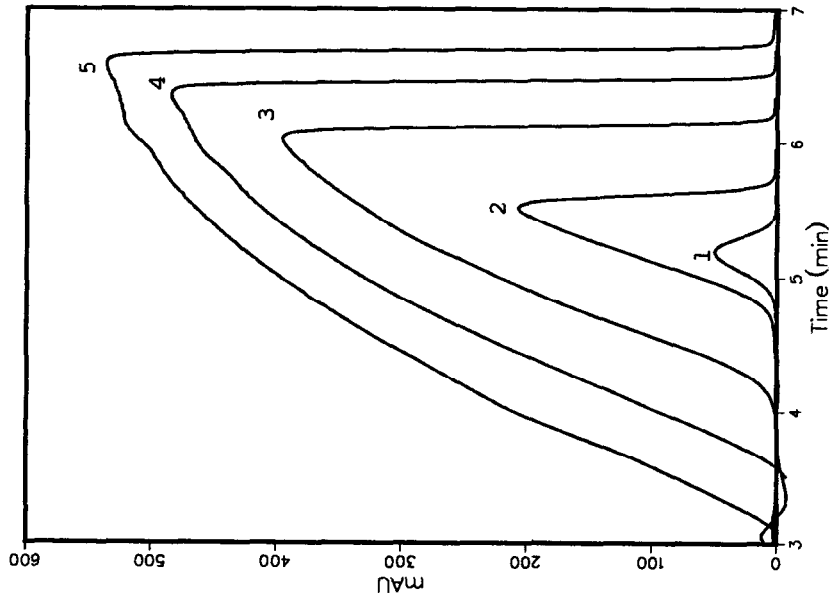


Fig. 13. Elution chromatograms of pulses of 2-phenylethanol of increasing sample size. UV detector (no response for the solvent). Experimental conditions as in Fig. 11, except 1% 2-propanol as strong solvent. 1, 0.2 μl; 2, 1 μl; 3, 5μl; 4, 10μl; 5, 15μl.

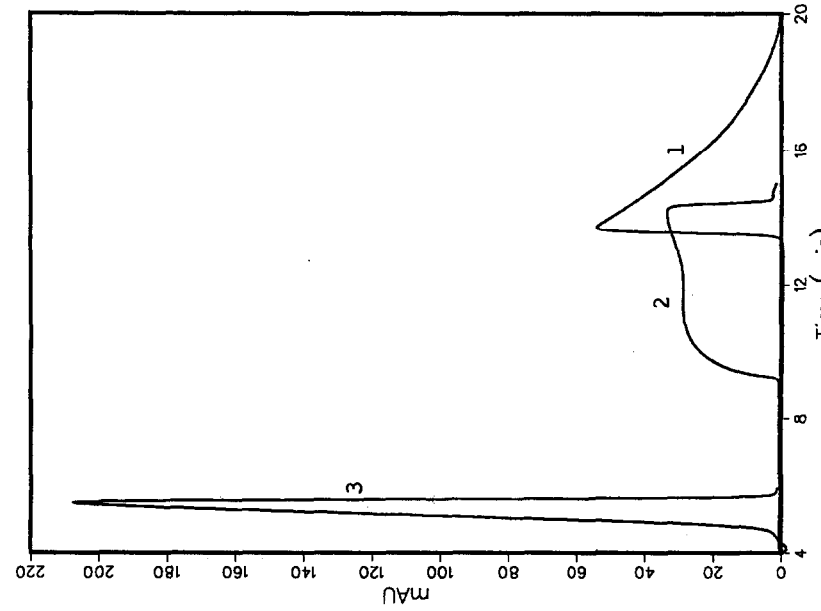
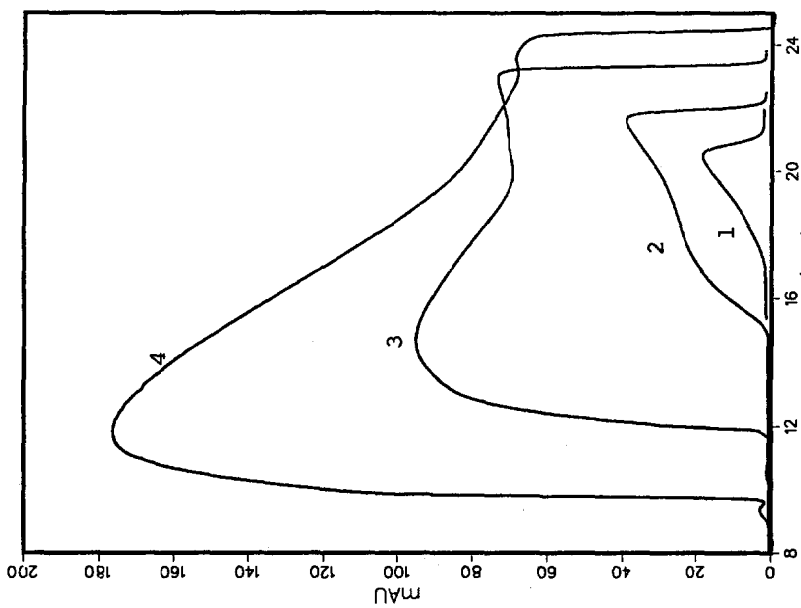


Fig. 14. Elution chromatograms of pulses of 2-phenylethanol of equal sample sizes (1 μl). UV detector (no response for the solvent). Experimental conditions as in Fig. 11, except variable concentration of the mobile phase in 2-propanol. 1, 0.1%; 2, 0.2%; 3, 1%.



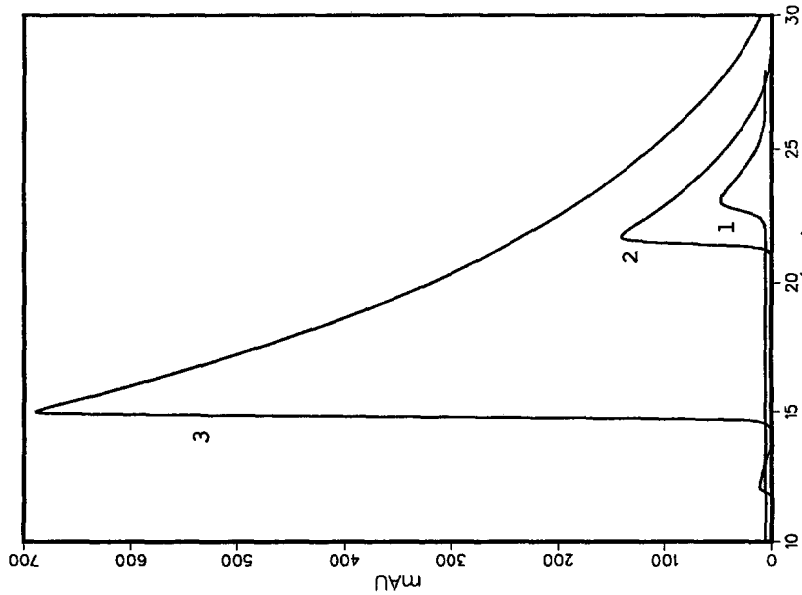


Fig. 15. Elution chromatograms of pulses of 3-phenyl-1-propanol of increasing sample size. UV detector (no response for the solvent). Experimental conditions as in Fig. 4, except 0.02% 2-propanol as strong solvent and detection wavelength 254 nm. 1, 0.2 μl; 2, 1 μl; 3, 10 μl.

Fig. 16. Elution chromatograms of pulses of 3-phenyl-1-propanol of increasing sample size. UV detector (no response for the solvent). Experimental conditions as in Fig. 15, except 0.1% 2-propanol as strong solvent. 1, 0.2 μl; 2, 1 μl; 3, 5 μl; 4, 10 μl.

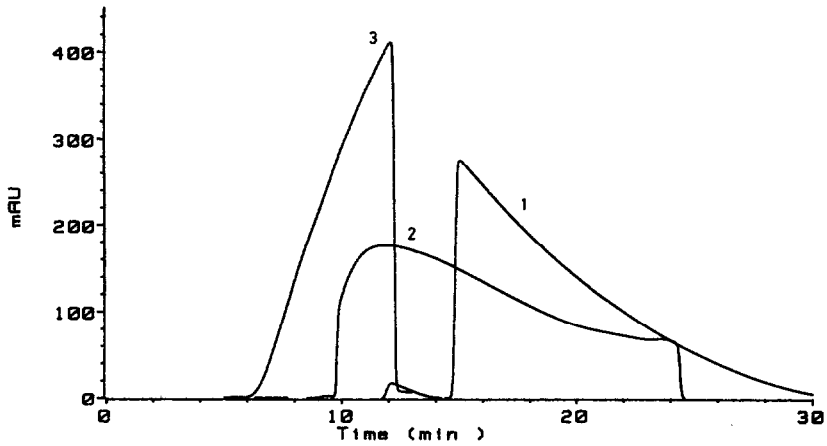


Fig. 17. Elution chromatograms of pulses of 3-phenyl-1-propanol of equal sample size (10 μl). UV detector (no response for the solvent). Experimental conditions as in Fig. 15, except variable concentration of the mobile phase in 2-propanol. 1, 0.02%; 2, 0.1%; 3, 0.4%.

not identical with) those observed with an anti-Langmuir isotherm. The bands are now leading, with a sharp rear boundary.

The dramatic character of the change in band profile with increasing concentration of the strong solvent in the mobile phase is illustrated by Fig. 14, which shows the band profiles obtained for the same amount of sample (1 μl of 2-phenylethanol) with three different mobile phases, containing 0.1, 0.2 and 1% 2-propanol. The marked decrease in retention time is obvious. The change in the profile is remarkable, as is the close agreement with the results of our theoretical study (see in ref. 1, Fig. 6).

Similar results were obtained with 3-phenyl-1-propanol under similar experimental conditions, although the numerical values are slightly different (see Figs. 15–17).

CONCLUSION

The results of this experimental investigation validate entirely the conclusion of the theoretical study[1]. The competition between the molecules of the strong solvent or other additives in the mobile phase and the components of the sample influence considerably the shape of the elution bands and probably the degree of resolution in addition to the production per unit time of a chromatographic column in preparative applications. It is indeed possible that a combination of additives could enhance the symmetry of the bands. It has been shown in the theoretical study that under some well defined set of experimental conditions the sample band could be both retained and eluted as a nearly symmetrical band. In this work we have not striven to duplicate these conditions, because we are interested in the profile of a single-component band only as an intermediate test of a complex theory.

Our work will be pursued by an investigation of the influence of the nature and strength of adsorption of the eluents compared with those of the solutes, of their

concentration and of the sample size, on the separation, yield and production rate for a binary mixture. This is the simplest problem of practical importance that the theoretician must tackle to the satisfaction of the chemical engineer.

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