Journal of Chromatography, 644 (1993) 239–252
Elsevier Science Publishers B.V., Amsterdam

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Studies on new cross-axis coil planet centrifuge for performing counter-current chromatography

III. Speculations on the hydrodynamic mechanism in stationary phase retention

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(First received November 24th, 1992; revised manuscript received March 30th, 1993)

ABSTRACT

Retention of the stationary phases of one organic–aqueous solvent system and three aqueous–aqueous polymer solvent systems was investigated on a cross-axis coil planet centrifuge. A graphic statistical treatment of all the data highlighted the prevailing effect of the inward–outward elution mode. A simplified model was proposed and studies on the paths and accelerations of cross-axis devices described in the previous paper provided explanations about the observed hydrodynamic behaviors.

INTRODUCTION

A series of experiments has been performed on the latest version of the cross-axis coil planet centrifuge (CPC) to measure retention of its stationary phase; those were described in Part I [1]. The results were obtained with one organic–aqueous and three aqueous–aqueous polymer two-phase solvent systems using a preparative single layer column. When the coil is mounted in the L position, retention of the stationary phase was found to be almost entirely governed by the inward–outward elution mode. The lighter mobile phase had to be eluted in the inward mode while the heavier mobile phase requires the use of the outward mode. When using the $X-1.5L$ position, such results apply to the three aqueous–aqueous polymer systems. The organic–aqueous system was also found to be dependent on the head–tail elution mode. Moreover the coil mounted in the L position produced a slightly higher retention of stationary phase than that used in the $X-1.5L$ position.

In this Part, statistics based on graphic studies are used to separate and evaluate the effects produced by each factor, *i.e.*, head–tail elution mode, inward–outward elution mode, direction of rotation and coil diameter. An explanation on the great influence of the inward–outward elution mode is given. Then the studies of Part II [2] are used to provide further explanations of the experimental observations.

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ANALYSIS OF PHASE RETENTION DATA

As described in Part I [1], the cross-axis coil planet centrifuge allows use of 5.5 cm and 10 cm diameter columns in the L or $X-1.5L$ positions. Table I (5.5 cm diameter) and Table II (10 cm diameter) list all the results for the L position, as Table III (5.5 cm diameter) and Table IV (10 cm diameter) for the $X-1.5L$ position. Each table shows the retention percentage of stationary phase inside the apparatus for four two-phase solvent systems with both upper and lower phases used as mobile phase. All the measurements were made with the short preparative columns (one layer, 5.5 and 10 cm hub diameter for 19.8 ml and 41.0 ml internal volumes) described in part I [1] and a 3 ml/min flow-rate at 800 rpm. With a fixed mobile phase, eight retention data are shown. They are expressed from three factors: the direction of planetary motion (P_I and P_{II}, as shown at the bottom of Table I); the head–tail elution mode (H = head-to-tail; T = tail-to-head); and the direction of elution along the axis of the column (I = inward; O = outward). These data are arranged from top to bottom in decreasing of phase retention. The measurements obtained with left-handed coils are shaded in the four tables.

TABLE I

RETENTION (%) OF STATIONARY PHASE IN 5.5-cm HELICAL DIAMETER COIL, L POSITION

Mobile phase	Solvent system[a]							
	1: 1-Butanol–0.13 M NaCl (1:1) containing 1.5% (w/v) HPC		2: PEG 1000 12.5%, K_2HPO_4 12.5%		3: PEG 8000 4.4%, dextran T500 7.0%		4: PEG 8000 4.0%, dextran T500 5.0%	
	Condition[b]	%	Condition	%	Condition	%	Condition	%
Upper	P_I-H-I	74.7	P_{II}-T-I	55.6	P_I-H-I	46.0	P_I-T-I	9.3
	P_{II}-T-I	74.2	P_I-H-I	53.0	P_{II}-T-I	43.4	P_{II}-H-I	8.8
	P_I-T-I	72.6	P_I-T-I	52.1	P_{II}-H-I	42.3	P_{II}-T-I	7.4
	P_{II}-H-I	63.3	P_{II}-H-I	40.9	P_I-T-I	40.0	P_I-H-I	3.6
	P_I-H-O	6.0	P_{II}-H-O	2.0	P_I-H-O	9.9	P_I-H-O	0
	P_{II}-H-O	0	P_I-H-O	0	P_{II}-H-O	9.5	P_{II}-H-O	0
	P_I-T-O	0	P_I-T-O	0	P_I-T-O	1.8	P_I-T-O	0
	P_{II}-T-O	0	P_{II}-T-O	0	P_{II}-T-O	0.5	P_{II}-T-O	0
Lower	P_I-T-O	75.8	P_{II}-H-O	62.1	P_{II}-H-O	8.4	P_I-H-O	6.8
	P_{II}-H-O	74.2	P_I-T-O	61.1	P_{II}-T-O	7.9	P_{II}-H-O	1.0
	P_{II}-T-O	72.6	P_I-H-O	55.8	P_I-H-O	6.1	P_{II}-T-O	0
	P_I-H-O	72.1	P_{II}-T-O	52.1	P_I-T-O	5.5	P_I-T-O	0
	P_I-T-I	4.2	P_I-T-I	7.4	P_{II}-H-I	1.9	P_{II}-H-I	0
	P_{II}-T-I	3.0	P_{II}-H-I	3.7	P_I-T-I	0	P_I-T-I	0
	P_{II}-H-I	1.9	P_{II}-T-I	3.0	P_{II}-T-I	0	P_{II}-T-I	0
	P_I-H-I	1.5	P_I-H-I	1.5	P_I-H-I	0	P_I-H-I	0

[a] Composition indicated in % (w/w) except the first one v/v; HPC = 1-hexadecylpyridinium chloride.

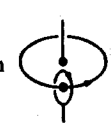
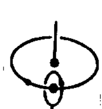
[b] P_I = Planetary motion ; P_{II} = planetary motion ; H = head to tail; T = tail to head; I = inward elution, O = outward elution; plain background = right-handed coil; shaded background = left-handed coil.

TABLE II

RETENTION (%) OF STATIONARY PHASE IN 10.0-cm HELICAL DIAMETER COIL, *L* POSITION

Mobile phase	Solvent system[a]							
	1: 1-Butanol–0.13 *M* NaCl (1:1) containing 1.5% (w/v) HPC		2: PEG 1000 12.5%, K_2HPO_4 12.5%		3: PEG 8000 4.4%, dextran T500 7.0%		4: PEG 8000 4.0%, dextran T500 5.0%	
	Condition[b]	%	Condition	%	Condition	%	Condition	%
Upper	[redacted]	61.0	[redacted]	45.4	[redacted]	37.1	[redacted]	0
	[redacted]	56.1	P_{II}-T-I	40.0	P_{II}-T-I	35.1	P_{II}-T-I	0
	P_{II}-T-I	53.7	P_I-H-I	35.6	[redacted]	34.1	[redacted]	0
	P_I-H-I	50.0	[redacted]	29.8	P_I-H-I	29.8	P_I-H-I	0
	P_{II}-H-O	13.9	P_I-T-O	11.7	P_I-T-O	21.5	P_I-T-O	0
	[redacted]	7.8	P_{II}-H-O	4.9	[redacted]	20.7	[redacted]	0
	P_I-T-O	6.3	[redacted]	2.4	[redacted]	14.6	[redacted]	0
	[redacted]	0	[redacted]	0	P_{II}-H-O	12.2	P_{II}-H-O	0
Lower	[redacted]	61.0	[redacted]	46.8	P_I-T-O	1.5	P_I-T-O	0
	[redacted]	59.8	P_{II}-H-O	39.0	P_I-H-I	0.7	P_I-H-I	0
	P_I-T-O	48.8	[redacted]	38.3	[redacted]	0	[redacted]	0
	P_{II}-H-O	48.3	P_I-T-O	36.6	[redacted]	0	[redacted]	0
	P_{II}-T-I	13.2	P_I-H-I	9.8	[redacted]	0	[redacted]	0
	[redacted]	9.0	[redacted]	8.5	[redacted]	0	[redacted]	0
	P_I-H-I	7.3	[redacted]	7.3	P_{II}-H-O	0	P_{II}-H-O	0
	[redacted]	3.7	P_{II}-T-I	6.1	P_{II}-T-I	0	P_{II}-T-I	0

[a,b] See footnotes in Table I.

The overall results show that the eight experimental conditions combined with the choice of mobile phase and the four two-phase solvent systems lead to different values for the retention of stationary phase. It is difficult to give a direct interpretation of all these results. Consequently, statistical methods were applied to assess the influence of each of the three factors (P_I–P_{II}, H–T or I–O) along with the diameter of the column (5.5 cm or 10 cm), the choice of mobile phase (lighter or heavier) and the position of the column (L or $X-1.5L$).

Two statistical methods have been applied to the measurements of retention of stationary phase. One is called "experimental design" [3] and allows an accurate estimation of the influence of each factor along with the possible interactions between these factors. The other method is based on graphic interpretations and was previously introduced by Ito [4]. Thus, the retention of stationary phase is plotted as one parameter is changed between the horizontal axis and the vertical axis. This is done for four factors: the planetary motion P_{II} *vs.* P_I (Figs. 1 and 2 for the L and $X-1.5L$ positions), the tail-to-head *vs.* the head-to-tail elution mode (Figs. 3 and 4 for the L and $X-1.5L$ positions), the outward *vs.* the inward elution mode (Figs. 5 and 6 for the L and $X-1.5L$ positions) and the 10.0 cm *vs.* the 5.5 cm diameter (Fig. 7 for L and $X-1.5L$ positions). Each figure includes a set of four graphs showing the retention of stationary phase in both 5.5 cm (A) and 10.0 cm (B) diameter columns with the upper (left) or the lower (right) phase used as the mobile phase, except for Fig. 7 involving four graphs with a mobile phase either heavier or lighter on both L and $X-1.5L$ positions.

Each graph is separated in four squares by thin horizontal and vertical lines. The upper right

TABLE III

RETENTION (%) OF STATIONARY PHASE IN 5.5-cm HELICAL DIAMETER COIL, $X-1.5L$ POSITION

Mobile phase	Solvent system[a]							
	1: 1-Butanol–0.13 *M* NaCl (1:1) containing 1.5% (w/v) HPC		2: PEG 1000 12.5%, K_2HPO_4 12.5%		3: PEG 8000 4.4%, dextran T500 7.0%		4: PEG 8000 4.0%, dextran T500 5.0%	
	Condition[b]	%	Condition	%	Condition	%	Condition	%
Upper	P_{I}-T-I	85.0	P_{I}-T-I	38.7	P_{I}-H-I	44.4	P_{II}-H-I	6.5
	P_{II}-T-I	74.7	P_{II}-H-I	36.0	P_{I}-T-I	35.3	P_{I}-T-I	2.8
	P_{I}-H-I	48.9	P_{I}-H-I	29.9	P_{II}-H-I	32.6	P_{I}-H-I	0
	P_{II}-H-I	45.8	P_{II}-T-I	20.1	P_{II}-T-I	32.3	P_{II}-T-I	0
	P_{I}-H-O	29.4	P_{II}-T-O	2.0	P_{I}-H-O	20.0	P_{I}-H-O	0
	P_{II}-H-O	26.2	P_{I}-H-O	1.6	P_{II}-H-O	14.1	P_{II}-H-O	0
	P_{II}-T-O	0	P_{II}-H-O	0.7	P_{II}-T-O	11.6	P_{II}-T-O	0
	PI-T-O	0	PI-T-O	0	P_{I}-T-O	0	P_{I}-T-O	0
Lower	P_{I}-H-O	60.8	P_{I}-H-O	55.0	P_{II}-H-O	8.0	P_{II}-T-O	4.7
	P_{II}-H-O	55.3	P_{II}-T-O	54.5	P_{I}-H-O	6.0	P_{II}-H-O	2.0
	P_{I}-H-I	40.3	P_{I}-T-O	24.4	P_{II}-T-O	2.8	P_{I}-H-O	0.9
	P_{II}-T-O	28.5	P_{II}-H-O	24.4	P_{II}-H-I	0	P_{II}-H-I	0.5
	P_{II}-H-I	26.8	P_{I}-T-I	3.7	P_{I}-T-I	0	P_{I}-T-I	0
	P_{I}-T-O	5.3	P_{II}-H-I	3.0	P_{I}-T-O	0	P_{I}-T-O	0
	P_{I}-T-I	2.0	P_{II}-T-I	1.4	P_{I}-H-I	0	P_{I}-H-I	0
	P_{II}-T-I	1.7	P_{I}-H-I	1.0	P_{II}-T-I	0	P_{II}-T-I	0

[a,b] See footnotes in Table I.

square indicates a satisfactory retention of stationary phase for the two values of the studied parameter. The most important information is provided by the thick diagonal line that separates the diagram into two triangles. The data points located on or near the diagonal line indicate the studied effect has no influence on the retention of the stationary phase. The deviation of the point from that diagonal line indicates an effect of the studied parameter, whose relative magnitude is shown by the distance between the point and the diagonal line. Each graph contains 16 points corresponding to the four solvent systems and the four combinations between the two remaining factors. The points are numbered from 1 to 4 to show the solvent system used (see tables for identification).

Fig. 1A consists in a pair of graphs showing the retention of stationary phase with a column in the *L* position for P_{II} *vs.* P_{I}, for the upper (left) and the lower (right) phases used as mobile phase. Each point is displayed as a specific symbol, *i.e.*, open circle for the head-to-tail elution mode and solid circle for the tail-to-head mode with arrows indicating the inward elution mode if directed toward the right and the outward mode if directed toward the left. All the points are very close to the diagonal line with either the upper or the lower phase as a mobile phase. It demonstrates the direction of planetary motion P_{I} or P_{II} has little effect on the retention of stationary phase with the 5.5 cm diameter column. Fig. 1B also shows that no effect appears with the 10.0-cm diameter column as all

TABLE IV

RETENTION (%) OF STATIONARY PHASE IN 10.0-cm HELICAL DIAMETER COIL, $X-1.5L$ POSITION

Mobile phase	Solvent system[a]							
	1: 1-Butanol–0.13 *M* NaCl (1:1) containing 1.5% (w/v) HPC		2: PEG 1000 12.5%, K_2HPO_4 12.5%		3: PEG 8000 4.4%, dextran T500 7.0%		4: PEG 8000 4.0%, dextran T500 5.0%	
	Condition[b]	%	Condition	%	Condition	%	Condition	%
Upper	[redacted]	81.7	[redacted]	37.3	[redacted]	34.1	[redacted]	0
	P_{II}-T-I	57.1	P_{II}-T-I	21.5	P_{I}-H-I	30.2	P_{I}-H-I	0
	[redacted]	40.2	P_{II}-H-O	14.1	P_{II}-T-I	20.5	P_{II}-T-I	0
	P_{I}-H-I	37.1	P_{I}-H-I	12.2	P_{I}-T-O	19.8	P_{I}-T-O	0
	P_{II}-H-O	26.8	P_{I}-T-O	11.7	[redacted]	14.1	[redacted]	0
	[redacted]	18.3	[redacted]	4.9	[redacted]	9.8	[redacted]	0
	P_{I}-T-O	4.9	[redacted]	0	[redacted]	8.5	[redacted]	0
	[redacted]	0	[redacted]	0	P_{II}-H-O	2.4	P_{II}-H-O	0
Lower	[redacted]	60.5	P_{II}-H-O	41.5	P_{II}-H-O	3.4	P_{II}-H-O	0
	P_{II}-H-O	46.8	[redacted]	31.2	[redacted]	0	[redacted]	0
	P_{I}-H-I	44.9	P_{I}-H-I	28.3	P_{I}-H-I	0	P_{I}-H-I	0
	[redacted]	30.5	P_{I}-T-O	19.5	P_{I}-T-O	0	P_{I}-T-O	0
	[redacted]	20.7	[redacted]	8.8	[redacted]	0	[redacted]	0
	P_{I}-T-O	6.3	P_{II}-T-I	3.9	P_{II}-T-I	0	P_{II}-T-I	0
	P_{II}-T-I	3.7	[redacted]	3.4	[redacted]	0	[redacted]	0
	[redacted]	2.4	[redacted]	0	[redacted]	0	[redacted]	0

[a,b] See footnotes in Table I.

the points stay as close as they were for the smaller diameter. Fig. 2A shows the same lack of effect, except for the 1-butanol–0.13 *M* $NaCl_{aq}$ (+HPC) system. Its retention of stationary phase is enhanced by the combination of the P_I planetary motion and the tail-to-head elution mode with the a mobile upper phase or the P_{II} planetary motion and the tail-to-head elution mode with a mobile lower phase, whatever the diameter may be. No effect is involved in the head-to-tail elution mode with the 5.5 cm diameter column, whereas the P_{II}-H (upper phase mobile) and P_I-H (lower phase mobile) combinations increase the retention of stationary phase with the 10.0 cm diameter.

All the points in Fig. 3A and B are close to the diagonal line. The head-to-tail or tail-to-head elution modes consequently have no effect on the retention of stationary phase with a column in the L position. Neither does Fig. 4A characterize a real effect of the (H) or (T) elution modes. However, Fig. 4B illustrates a general effect of the head-to-tail or tail-to-head elution mode. With few exceptions, the combinations of upper phase mobile/tail-to-head and lower phase mobile/head-to-tail lead to the best retention of stationary phase in a 10.0-cm diameter column in the $X-1.5L$ position.

Fig. 5A and B show a strong effect of the inward/outward elution mode. All the points are located either below the diagonal line if the upper phase is mobile and above, if the lower phase is mobile. This indicates that for both diameters the best retention of stationary phase is obtained with the upper phase used as the mobile phase with the inward mode or the mobile lower phase with the outward mode. The same effects are shown on Fig. 6A and B. They are weaker compared to that shown for the *L* position. The stationary phase retention is thus

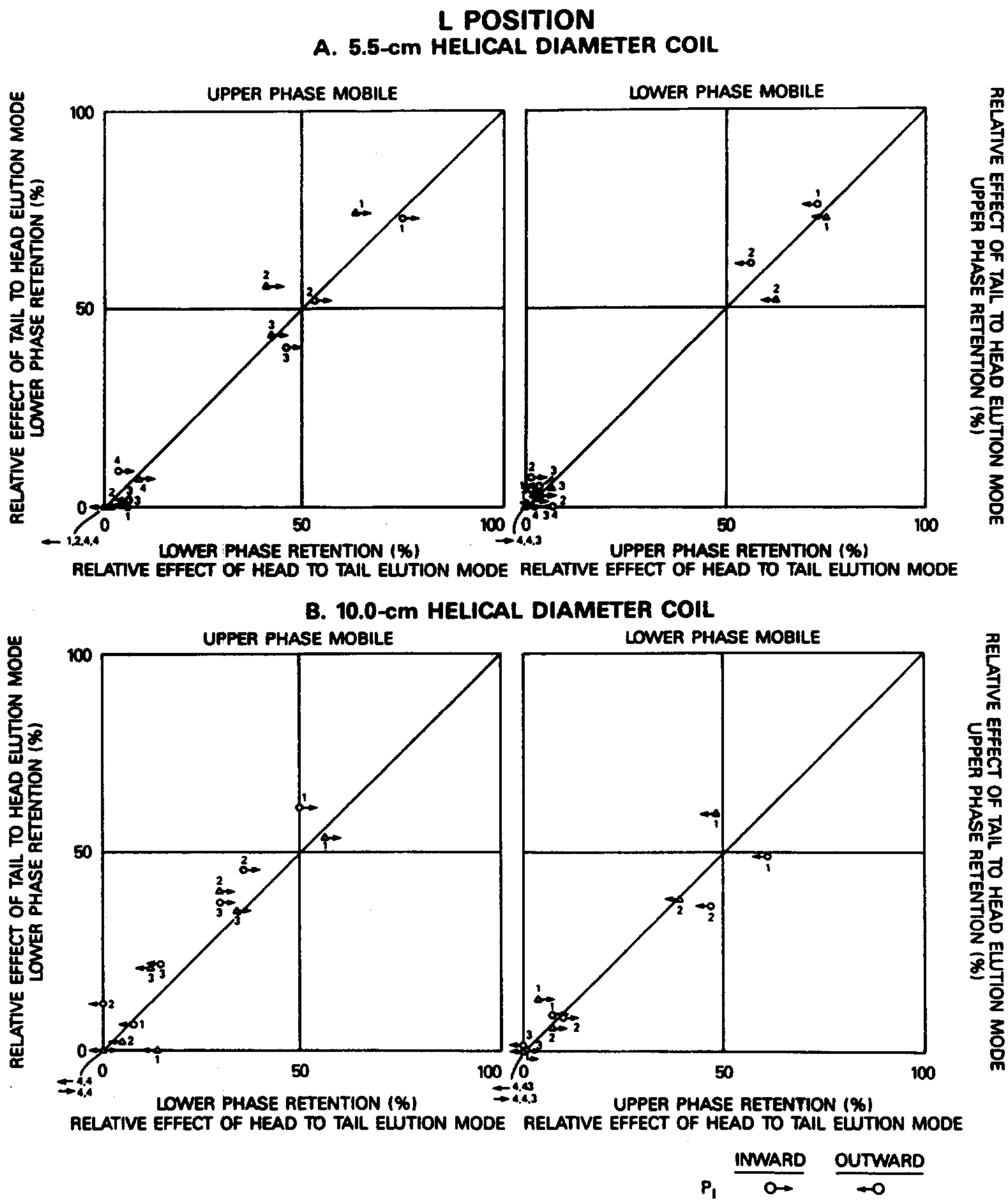


Fig. 1. L position: effects of planetary motion P_I and P_{II} on the retention of the stationary phase. (A) 5.5-cm helical diameter coil; (B) 10.0-cm helical diameter; left: upper phase mobile; right: lower phase mobile.

enhanced by the combinations of upper phase mobile/inward mode and lower phase mobile/outward mode, whatever the position and the diameter of the column.

Fig. 7 illustrates the influence of the column diameter. All the points with a retention of stationary phase higher than 20% are located below the diagonal line for both upper and lower phases as mobile. The 5.5 cm diameter consequently enhances the retention of stationary phase for both L and $X-1.5L$ positions. When the upper phase is chosen as mobile with the L position, the data points corresponding to at least 20% of retention have the arrows directed

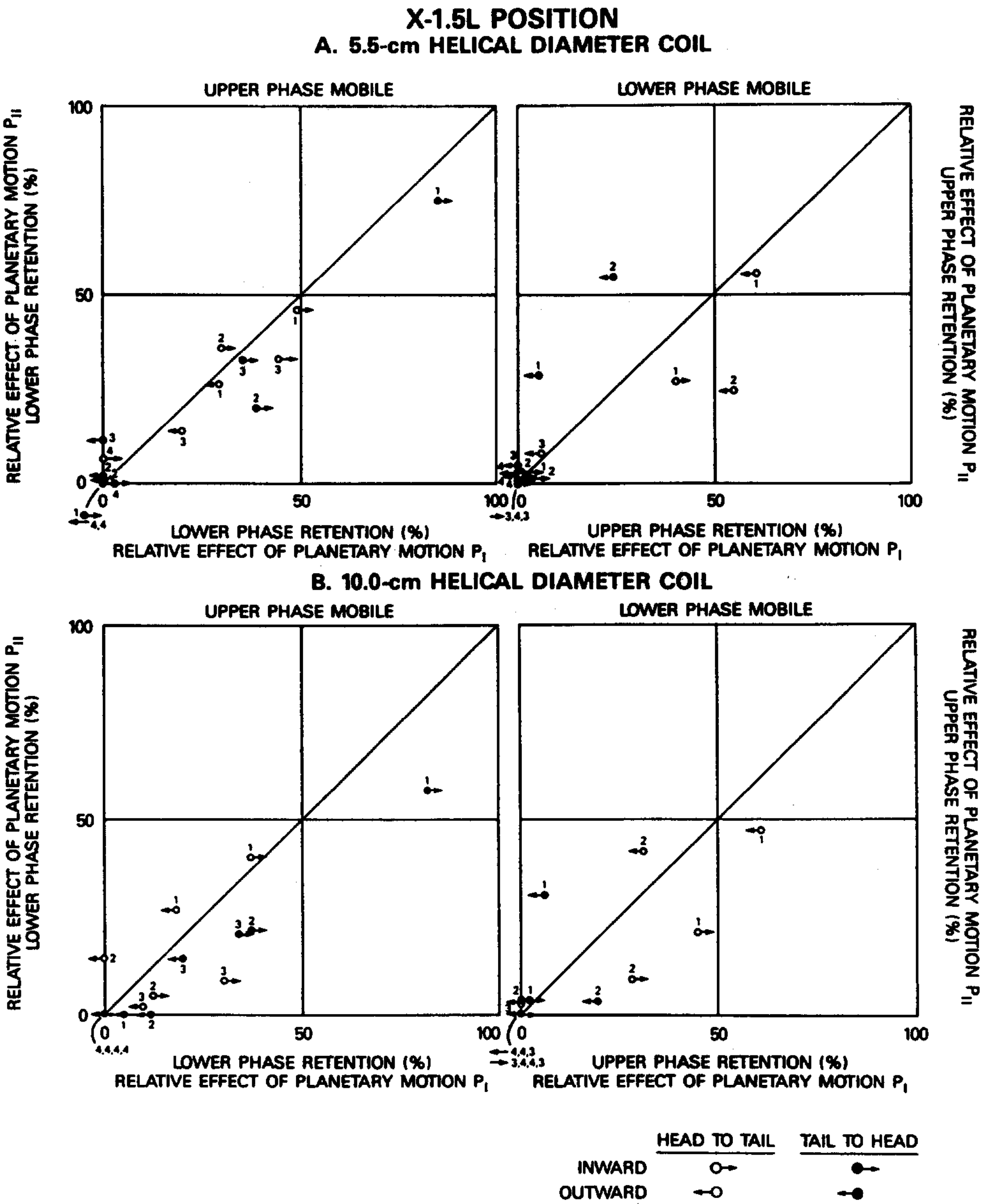


Fig. 2. $X-1.5L$ position: effects of planetary motion P_I and P_{II} on the retention of the stationary phase. (A) 5.5-cm helical diameter coil; (B) 10.0-cm helical diameter; left: upper phase mobile; right: lower phase mobile.

toward the right. Sufficient retention of stationary lower phase is thus achieved with the inward elution mode, while the use of stationary upper phase profits by the outward elution mode. These observations are correlated with the conclusions derived from Fig. 5 illustrating the effects of the inward–outward elution mode. The data points corresponding to the $X-1.5L$ position do not all show the same arrow direction, pointing out the weaker effect of the inward–outward elution mode for this position.

The above analysis shows the relative importance of all the factors studied and their possible interactions. The inward–outward factor is the

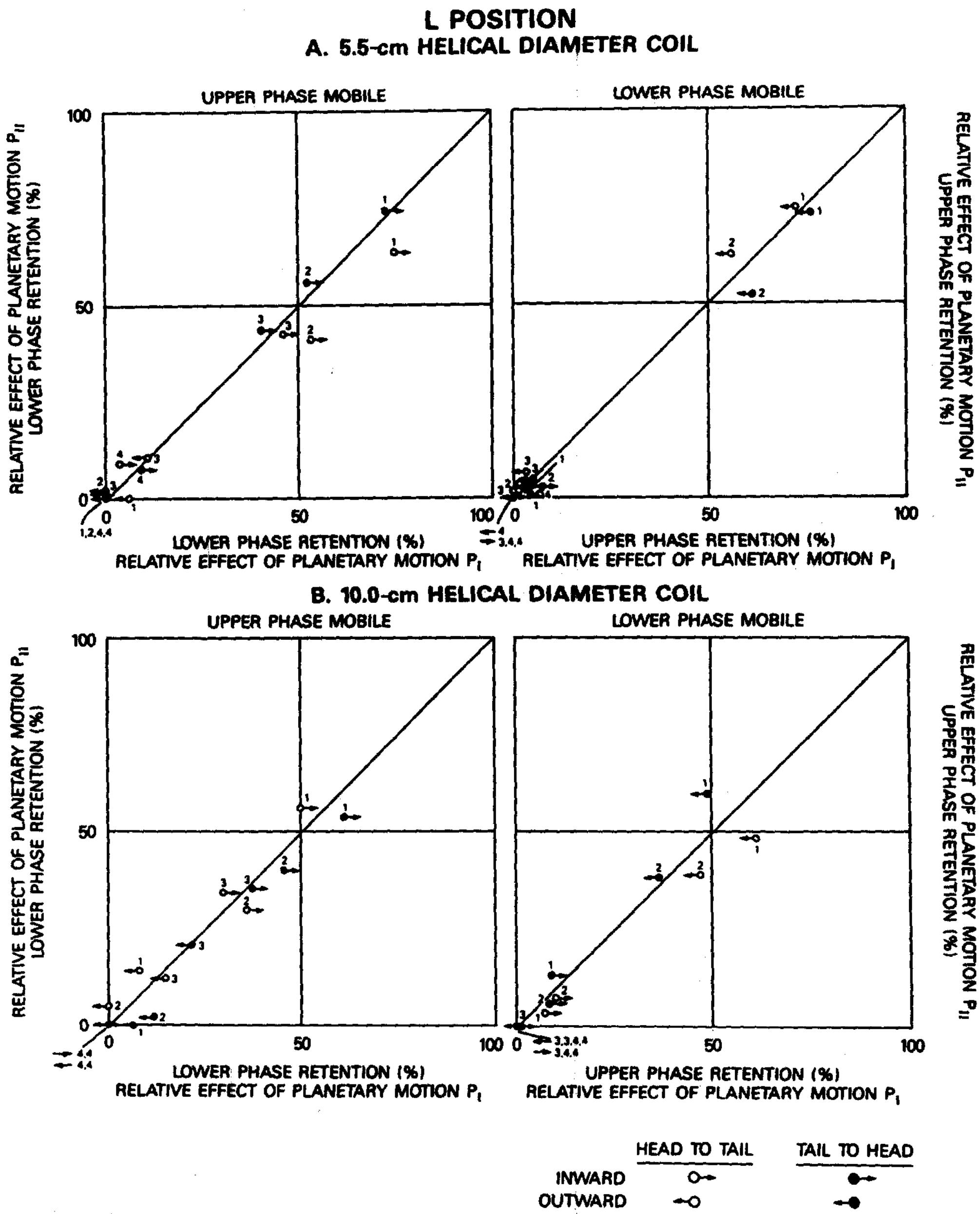


Fig. 3. L position: effects of the head–tail elution mode on the retention of the stationary phase. (A) 5.5-cm helical diameter coil; (B) 10.0-cm helical diameter; left: upper phase mobile; right: lower phase mobile.

strongest among those studied and it is correlated only with the choice of mobile phase to enhance the retention of stationary phase. For both diameters, *i.e.*, 5.5 cm and 10.0 cm, and for both positions, *i.e.*, L and $X-1.5L$, the highest levels of retention of stationary phase are obtained with an upper mobile phase pumped in the inward direction or a lower mobile phase pumped in the outward direction.

The diameter of the coil is also an important factor since the retention is increased by use of the 5.5 cm coil whatever the values of the other parameters. The head–tail elution modes and the direction of planetary motions P_I and P_{II}

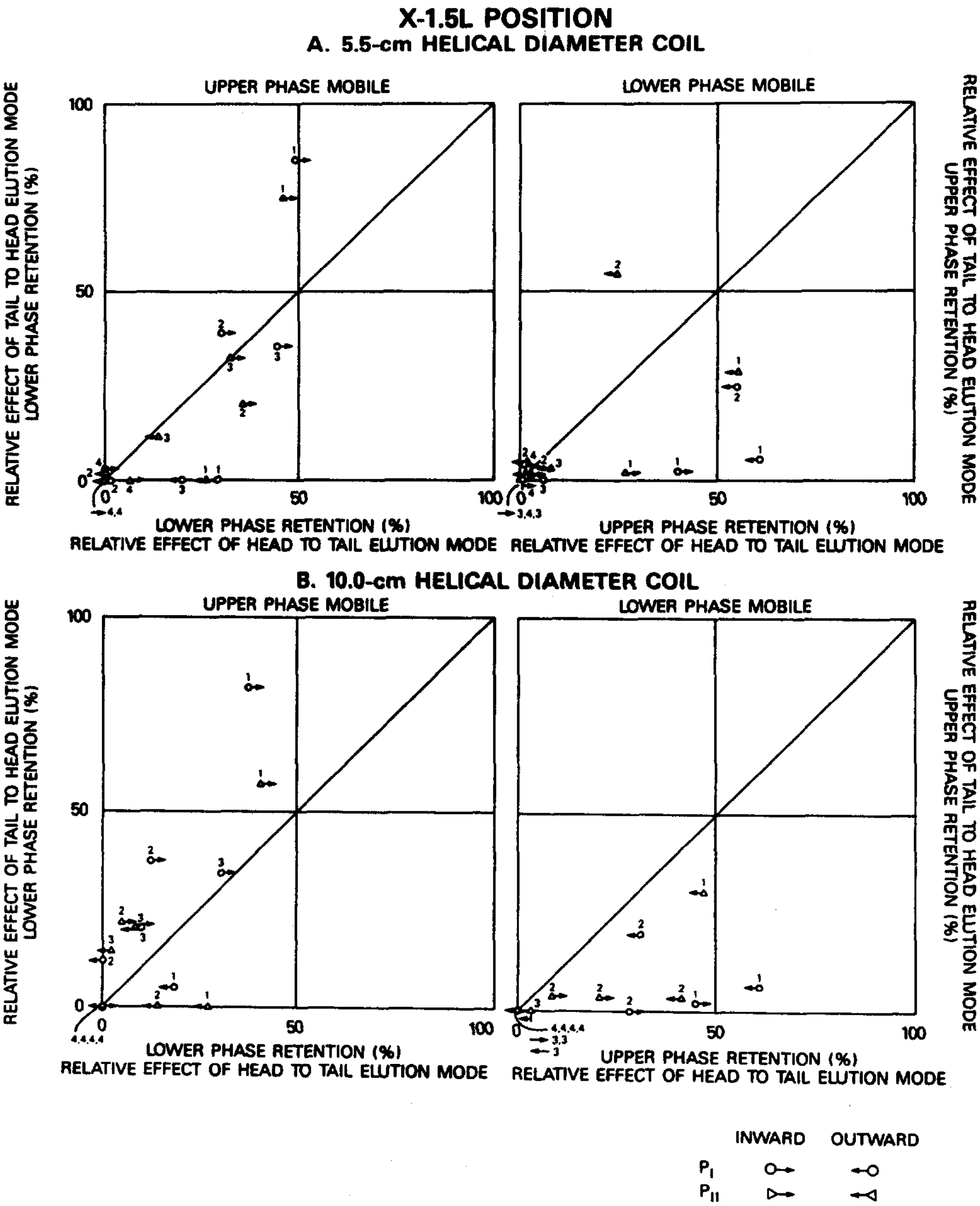


Fig. 4. $X-1.5L$ position: effects of the head–tail elution mode on the retention of the stationary phase. (A) 5.5-cm helical diameter coil; (B) 10.0-cm helical diameter; left: upper phase mobile; right: lower phase mobile.

have no effects with the L position. The head–tail factor has an effect only with the 10.0 cm coil in the $X-1.5L$ position: the best combinations are the mobile upper phase pumped in the tail-to-head mode or the mobile lower phase in the head-to-tail mode. The direction of planetary motion has an even more restricted effect as it applies only to the 1-butanol–0.13 M $NaCl_{aq}$ (+HPC) system with the $X-1.5L$ position of the coil. When the upper phase is mobile, the P_I-T for 5.5 cm diameter and the P_I-T and P_{II}-H for 10.0 cm lead to the best retention of stationary phase. For the lower phase mobile, the P_{II}-T for 5.5 cm diameter and P_{II}-T and P_I-H for 10.0

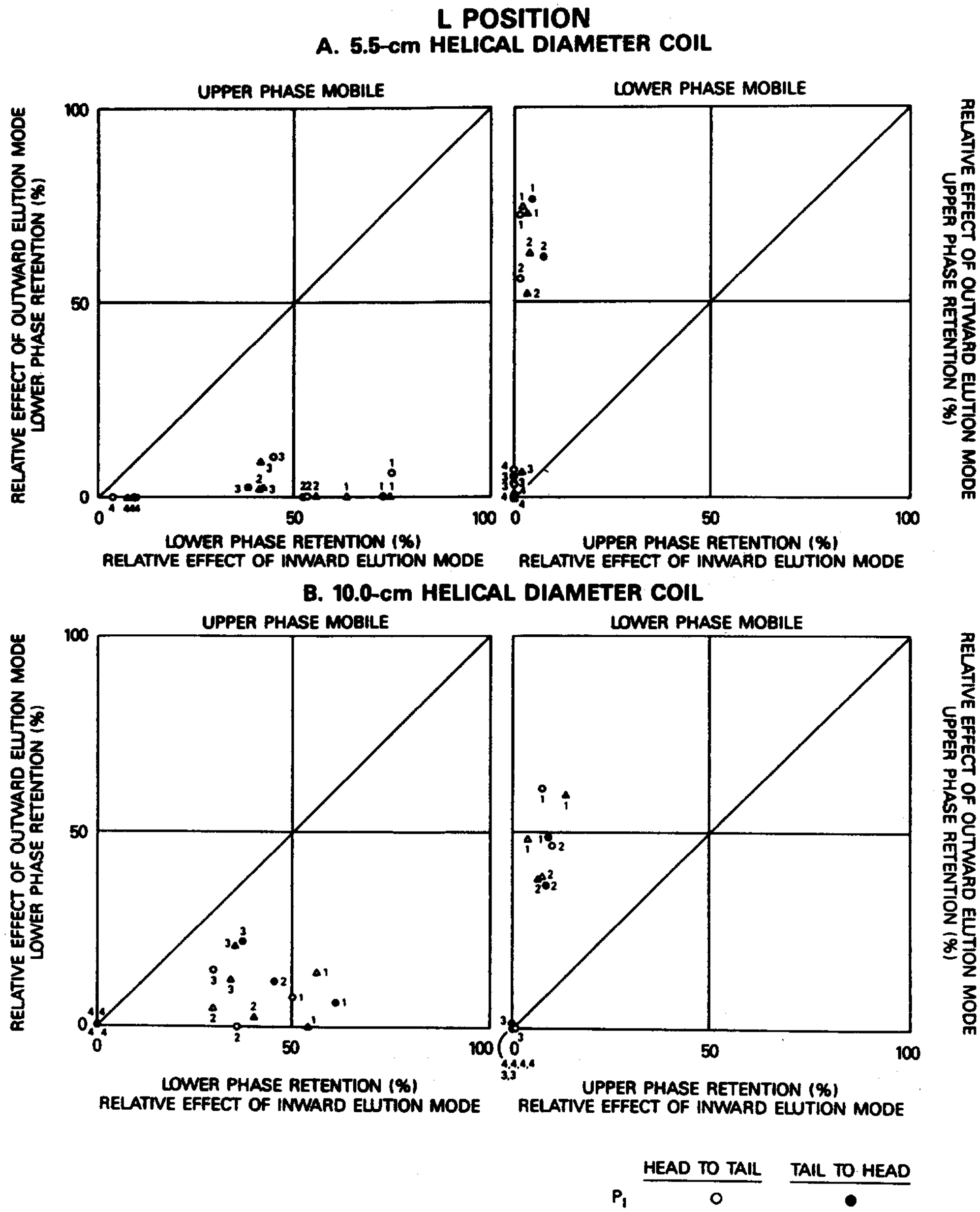


Fig. 5. *L* position: effects of the inward–outward elution mode on the retention of the stationary phase. (A) 5.5-cm helical diameter coil; (B) 10.0-cm helical diameter; left: upper phase mobile; right: lower phase mobile.

cm enhance the retention. The effect of the coil position was not studied but the overall retention measurements suggest that its influence is very small with the 5.5 cm diameter while the *L* position enhances retention for the 10.0 cm diameter.

Consequently, to achieve the highest retention of stationary phase, the three aqueous–aqueous two-phase polymer systems (numbered 2, 3 and 4) require the 5.5-cm coil with the mobile upper phase pumped inward or the mobile lower phase

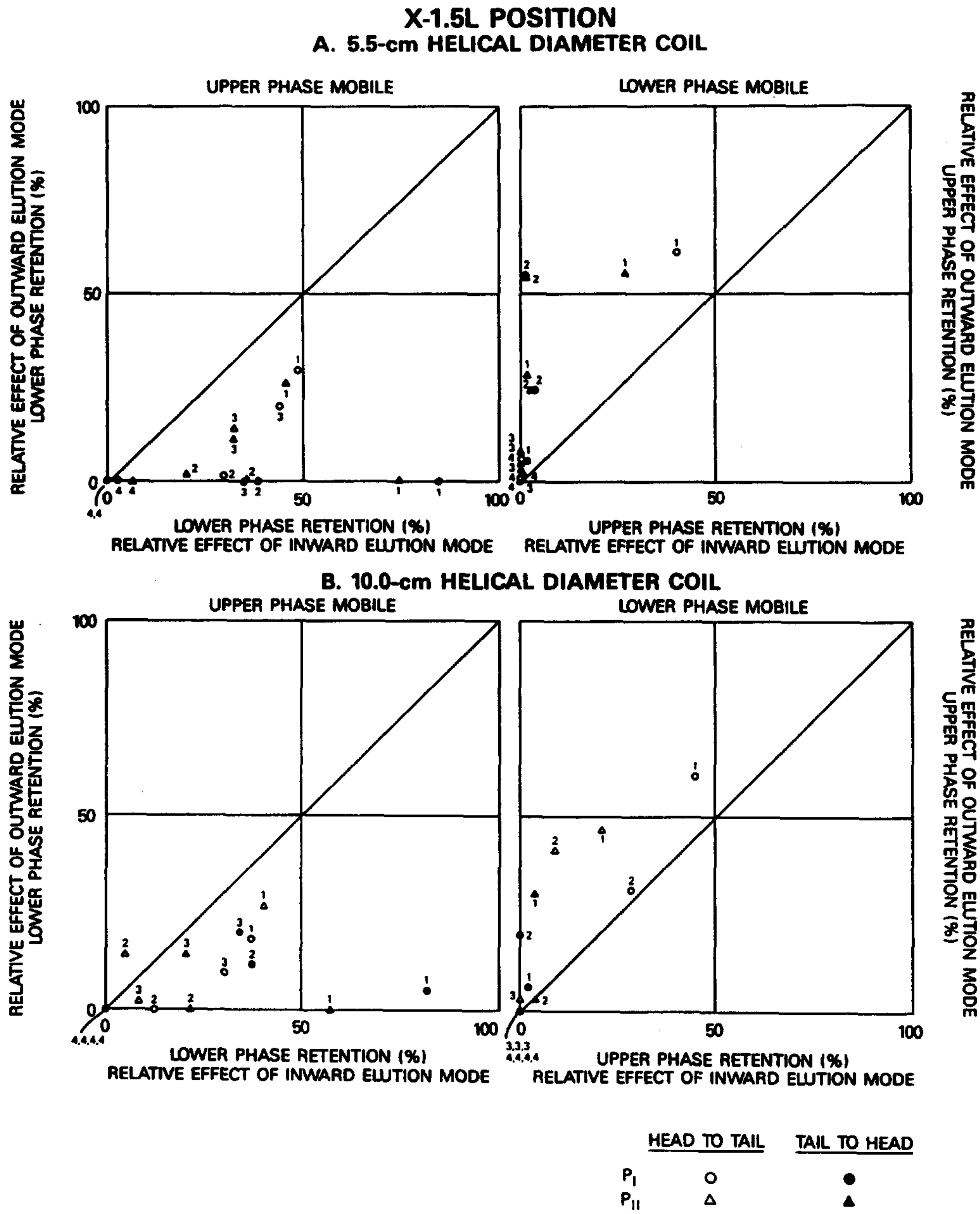


Fig. 6. $X-1.5L$ position: effects of the inward–outward elution mode on the retention of the stationary phase. (A) 5.5-cm helical diameter coil; (B) 10.0-cm helical diameter; left: upper phase mobile; right: lower phase mobile.

pumped outward with either the L or $X-1.5L$ coil positions. For the first solvent system, made of an organic solvent mixed with an aqueous phase, the L position requires the same combinations as with the other solvent systems. However, the $X-1.5L$ position requires more precise combinations: P_I-T-I for the upper phase as mobile and P_{II}-T-O for the lower phase as mobile with a 5.5-cm diameter coil.

These results are correlated with those previously obtained with a type X-LL cross-axis CPC

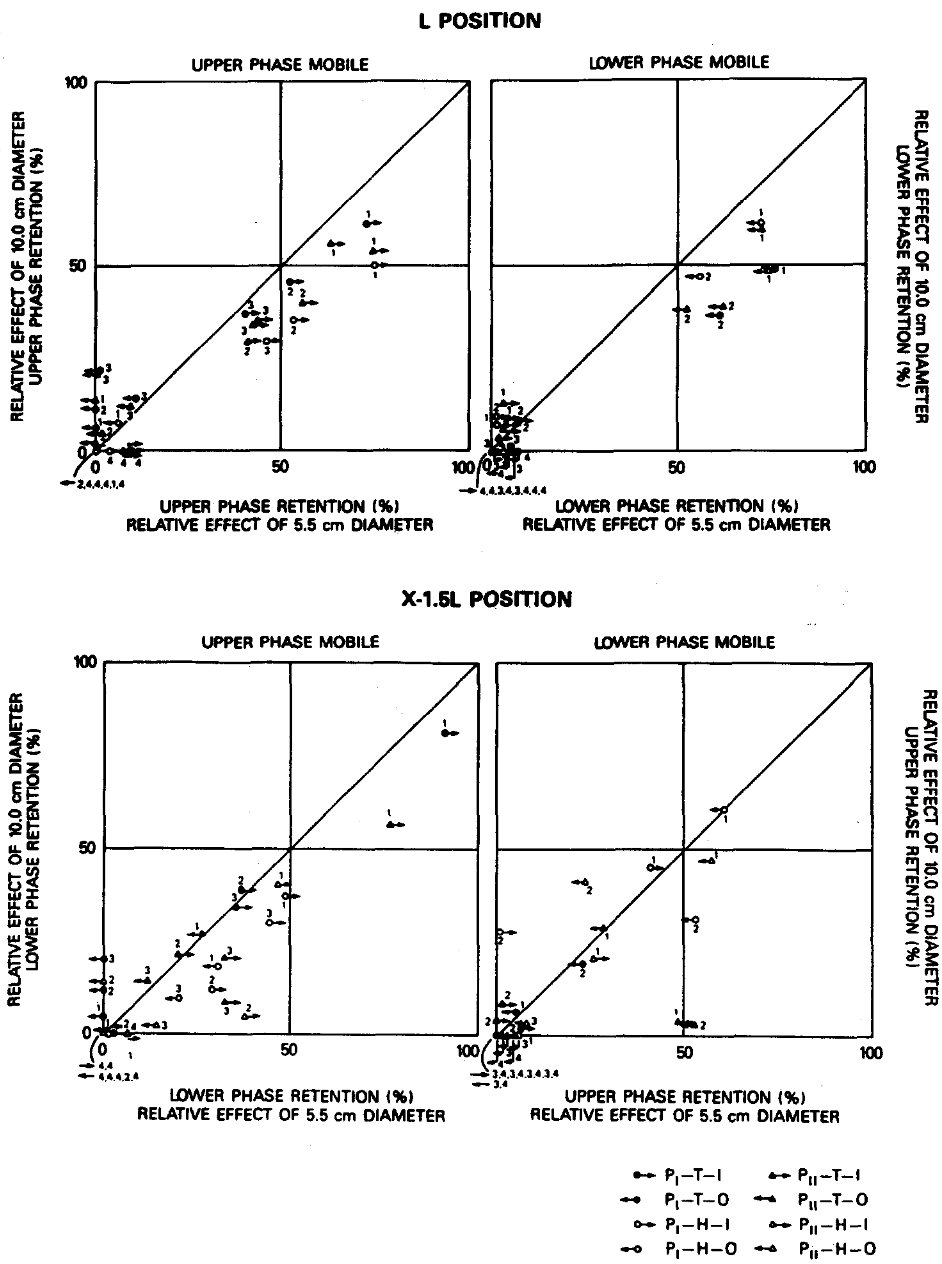


Fig. 7. Effects of the helical coil diameters with L and $X-1.5L$ positions on the retention of the stationary phase; left: upper phase mobile; right: lower phase mobile.

[4,5]. There it was concluded that the highest retention of stationary phase is obtained with the upper phase as mobile and the P_I-T-I and P_{II}-H-I combination or with the lower phase as mobile and the P_{II}-T-O and P_I-H-O combination. These results are similar to the requirements obtained with the 1-butanol–0.13 M $NaCl_{aq}$ (+HPC) system with the $X-1.5L$ position, except they allow the choice of two combinations instead of one when the mobile phase is chosen. For the aqueous–aqueous polymer systems (not studied on the previous X-LL prototype), the require-

ments are shared with these for organic/aqueous systems between the two cross-axis prototypes but are less precise. Consequently, the head–tail elution mode and the direction of planetary motion show no effect with aqueous–aqueous polymer two-phase systems while they have an influence on organic–aqueous two-phase systems.

SPECULATION ON THE HYDRODYNAMIC MECHANISM

Fig. 8 is intended to explain the strong correlation between the inward–outward elution mode and the choice of the mobile phase. When the lighter phase is mobile, the best retention of stationary phase is achieved with the inward elution mode, *i.e.*, from the outside end to the inside end of the column. Such a behavior is explained in Fig. 8. The descriptive model is highly simplified: it assumes the two phases are completely separated along the column, the heavier one accumulating toward the outside end of the column, pushing the lighter phase toward

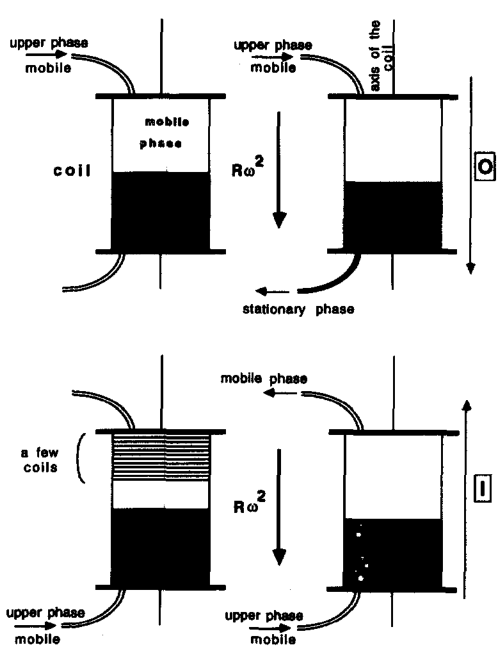


Fig. 8. Influence of the inward–outward elution mode on the retention of the heavier stationary phase inside a coil.

the inside end of the column. This model should be close to actual behavior inside columns in the L position since the head–tail elution mode has no effect. It could also be applied to the $X-1.5L$ position as far as aqueous–aqueous polymer two-phase solvent systems are considered, where no head–tail effect is involved. In the first case, the mobile phase is pumped in the outward mode. The small volumes of lighter phase continuously brought inside the column can not go through the heavier phase because they would migrate against centrifugal forces exerted in the heavier phase. Consequently, small amounts of the heavier phase are expelled from the column. In the other case, the lighter phase is introduced at the outside end of the column. The small volume of this phase continuously introduced in the column goes through the heavier phase due to a motion induced by the centrifugal forces inside the latter. As a result, the inward elution mode for the lighter mobile phase leads to better retention of the heavier stationary phase as observed in all of the experiments. However, the outward elution mode for the lighter mobile phase is able to provide a good retention of the stationary phase for some cases [*e.g.*, 1-butanol–0.13 M $NaCl_{aq}$ (+HPC) system in the 5.5-cm coil in the $X-1.5L$ position and the P_I-T-O mode, leading to 30% of retention]. At least two explanations are available. One is that the column is made of many coils slowing the leakage of heavier phase in the first case and possibly allowing the lighter phase to go through the heavier one. The second possibility is that the model may not apply as well to the coil in the $X-1.5L$ position: the head–tail elution mode intervenes for the 1-butanol–0.13 M $NaCl_{aq}$ (+HPC) system. Consequently, the Archimedes' screw force may interact with the centrifugal force in the model, leading to lack of separation of the phases along the column. Such a simplified model also applies to a mobile heavier phase and a stationary lighter one. When the Archimedes' screw force appears to be small, as for coils in the L position, the model is more applicable and indeed, no reliable exceptions are shown in Tables I and II.

An analysis of the paths and the accelerations induced by cross-axis CPCs was performed in

Part II [2]. All of the parametric equations were used to plot the paths and forces induced by a column in the L and $X-1.5L$ positions. The results showed that the paths are very similar for both coil positions: they appear as a circular path with a small deformation out of the rotation plane. The induced forces were separated into two perpendicular components relative to the tube of the coil, one in the plane of the coil, the other perpendicular to that plane and in one tangential component, in the plane of the coil. The relative importance of the tangential force over the two combined perpendicular forces was then studied for the cross-axis prototype with the L and $X-1.5L$ coil positions. Using the column in the L position, the tangential force inside the column compared to the added perpendicular forces represents up to 16.5% with the 10.0-cm diameter and up to 9% with the 5.5-cm diameter. For the column in the $X-1.5L$ position, this tangential force represents up to 90% with the small diameter and up to 125% with the large diameter of the combined perpendicular force. Such values explain the influence of the coil diameter. According to Fig. 7, the 5.5-cm coil diameter enhances retention of the stationary phase for both L and $X-1.5L$ positions. This can be correlated with the relative influence of the lateral force for each position; when the diameter is increased from 5.5 cm to 10.0 cm, the lateral force is increased in value compared to the perpendicular forces. Consequently, the role of the latter is lowered; as they take part to the retention of the phases inside the column, the retention of the stationary phase decreases. However, this explanation cannot be applied between two coil positions as they induce different force field geometries. For instance, the first solvent system can be retained up to 76% in a 5.5 cm diameter coil in the L position and up to 85% with the same coil in the $X-1.5L$ position while the relative influence of the tangential force are 9% and 90%, respectively. One reason for this effect could be the greater role of the unilateral distribution tendency [6,7] involved with the $X-1.5L$ position as shown by the influence of the head-to-tail or tail-to-head elution mode.

However as this tendency is not understood, a precise explanation on the effects of all the studied factors may be available only after a thorough mathematical analysis of the results [8]. Other experiments must be studied with the same solvent systems previously used on the X-LL cross-axis prototype [4].

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