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THE APPLICABILITY OF LIQUID–LIQUID SYSTEMS IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

J. P. CROMBEEN*, S. HEEMSTRA and J. C. KRAAK
Laboratory for Analytical Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

SUMMARY

Several types of liquid–liquid system were tested as phase systems in high-performance liquid chromatography. The stationary phase is generated on prepacked silica columns by pumping through the mobile phase which is presaturated with the stationary phase (*in situ* coating technique). The amount of stationary phase generated, the phase ratio and the reproducibility of retention data were determined. The effect of the column and reservoir temperature on the phase ratio and retention was extensively investigated. Although *in-situ*-generated liquid–liquid systems need more care than other common liquid chromatographic phase systems, such as extensive presaturation of the mobile phase and precise thermostatting of the stock reservoir and column, the results demonstrate that such systems are applicable in high-performance liquid chromatography. This is illustrated with a number of separations of text mixtures of various classes of compounds.

INTRODUCTION

Interest in applying liquid–liquid partition in high-performance liquid chromatography (HPLC), which was evident in the late 1960s[1,2], has drastically declined since the introduction of chemically bonded stationary phases. Their introduction overcame one of the main disadvantages of liquid–liquid systems, namely the mutual solubility of the two liquid phases which often gave rise to unstable phase systems. This is a pity, as liquid–liquid systems afford an almost unlimited potential for adjusting the degree and order of separations, because of the enormous number of liquid–liquid systems that can be devised. Moreover, liquid–liquid systems are thermodynamically very well defined and exactly reproducible. This in contrast to the chemically bonded stationary phases, which vary from supplier to supplier and sometimes even from batch to batch[3,4]. Furthermore, with liquid–liquid systems a phase ratio 10–20 times larger can be obtained in comparison with chemically bonded phases, and this favours greater loadability[5]. For these reasons and because of the significant improvements in HPLC technology during the past decade a renewed attempt to apply liquid–liquid partition chromatography seems to be justified.

Although many liquid–liquid systems have been applied in thin-layer[6,7] and

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paper chromatography[8] only a few have been tested in column liquid chromatography. In most cases, use was made of the viscous stationary phases used in gas chromatography (GC), such as Carbowax[9], ODPN[10], Fractonitril[11], and propane-1,2-diol[12], in combination with alkanes as mobile phases. These stationary phases were coated on low-surface-area supports by the solvent evaporation technique commonly applied in GC, and then columns were dry- or slurry-packed[13]. For less viscous stationary phases, such as those obtained with ternary phase systems[1,2] and ion-pair partition systems[14–16], the stationary phase was loaded on the support, prepacked in a column, by means of an *in situ* or precipitation technique[17]. These two loading techniques have the disadvantage that the amount of stationary phase cannot easily be adjusted.

In our study, we have investigated the applicability of binary and ternary phase systems, applied by the *in situ* method of loading prepacked silica columns. In order to create the possibility of varying the amount of stationary phase (*i.e.* the phase ratio), the influence of the column temperature at constant solvent reservoir temperature on the phase ratio and retention of test solutes was investigated. The study included investigations of the reproducibility of the liquid–liquid systems and the influence of the silica support, and it demonstrates the applicability of liquid–liquid systems to a broad range of solutes.

EXPERIMENTAL

Apparatus

The liquid chromatographic set-up is shown schematically in Fig. 1. It consisted of a reciprocating membrane pump (Orlita, Giessen, F.R.G.); a flow-through manometer acting as a pulse damper; an injection valve (Rheodyne 70-10) and a variable-wavelength detector (LC 4, Pye Unicam, U.K.). The columns (150 × 4.6 mm I.D.) were made of stainless steel 316 and were fitted with a thermostatting jacket. The stock reservoir and column jacket were connected to two separate thermostats (Haake, type F 4391, F.R.G.).

Materials

All solvents were obtained from commercial sources and were of analytical grade and used without pretreatment. The silica supports used were Hypersil (Shandon, U.K.) and LiChrosorb and LiChrospher (Merck, Darmstadt, F.R.G.).

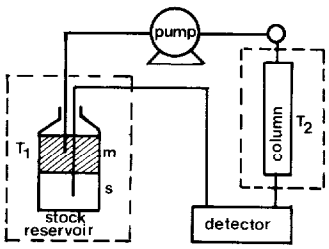


Fig. 1. Schematic representation of the experimental set-up used for the *in situ* generation of liquid–liquid systems.

Procedures

The silica columns were packed by a pressurized slurry technique with propanol as slurry liquid and methanol as pressurizing liquid. For large-surface-area silicas (Hypersil, LiChrosorb SI 100, LiChrospher SI 100) the maximal pressure was between 400 and 500 bar, and for smaller-surface-area silicas (LiChrospher SI 500 and SI 1000) a significantly lower filling pressure (between 150 and 180 bar) was used. The columns were washed with 50 ml of methanol, 50 ml of ethyl acetate and, finally, with the eluent until constant retention was achieved. The performance of all columns was tested in the adsorption mode by using hexane plus 0–5% ethyl acetate as mobile phase and butylbenzene, acetophenone and naphthalene as solutes.

The liquid–liquid systems were prepared by mixing both phases intensively for 12 h at a fixed temperature. For a number of systems the composition of both phases was determined by GC on OV-101 or Porapack as the stationary phases. The following systems were investigated:

(A) ethyl acetate–water

(B) chloroform–water–0.05 *M* ammonium formate (pH 3.0) (712:250:38, v/v)

(C) ethyl acetate–ethylene glycol (484:26, v/v)

(D) chloroform–hexane–formamide (90:9:1, v/v)

(E) iso-octane–ethanol–water (1185:766:49, v/v)

The total porosity of the column (V_0) was determined in various ways:

(1) From the weight difference of the column when filled with solvents of different density (usually ethyl acetate and chloroform);

(2) From the elution volume of an unretained solute under adsorption mode conditions;

(3) From analysis of the amount of neat solvent in the column after displacement with a more polar solvent.

In all cases, corrections were made for the volumes contributed by tubing, cell, sample loop, etc. The volume of the stationary phase (V_s) was then calculated by difference of the total porosity of the column and the actual retention volume of the unretained solute (V_0).

RESULTS AND DISCUSSION

In liquid–liquid chromatography the stationary phase is immobilized on a solid support. As solutes can also be adsorbed on this support, retention can be expected to be due to at least two contributions; adsorption and partition:

$$k' = K_{ads} \cdot \frac{A_s}{V_m} + K_p \cdot \frac{V_s}{V_m} \quad (1)$$

in which k' = capacity ratio, A_s = surface area of the support, K_{ads} = adsorption coefficient, K_p = liquid–liquid partition coefficient and V_m = volume of the mobile phase.

The contribution of adsorption to the overall retention of solutes depends on the surface area of the support and on the degree of liquid loading with the stationary phase. By selecting the proper support (*i.e.* surface area) and degree of liquid loading,

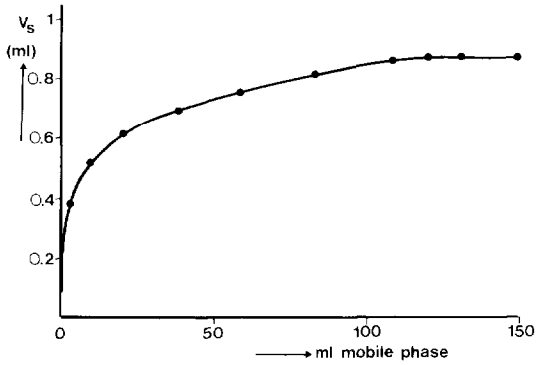


Fig. 2. Generation of the stationary phase as function of the volume of mobile phase pumped through the column. Column support, Hypersil; Phase system, B.

adsorption effects can usually be kept small. In that case, there will be a proportional relationship between k' and the phase ratio V_s/V_m.

We decided to investigate phase systems that allow the generation of a stationary phase via the saturated mobile phase, as this offers the opportunity to start with an efficient prepacked column.

In-situ-generated liquid–liquid systems

It is known[2,18] that binary and ternary systems containing water are suitable for generating liquid–liquid systems on prepacked silica columns. Various systems (see Experimental) were investigated for their applicability as *in-situ*-generated phase systems in column chromatography. In all cases, the generation of the amount of stationary phase was followed as a function of the volume of saturated mobile phase pumped through the column. Fig. 2 shows such a time course for a ternary liquid–liquid system on a prepacked silica column (LiChrosorb SI 100). As can be seen, the amount of stationary phase increases steeply with the first 50 ml of mobile phase and

TABLE I

MAXIMUM PHASE RATIO OBTAINED WITH THE LIQUID LIQUID SYSTEMS INVESTIGATED ON VARIOUS SILICA GELS WHEN SOLVENT RESERVOIR AND COLUMN ARE KEPT AT THE SAME TEMPERATURE (USUALLY 22°C)

Support	A_s*	V_p**	*Liquid–liquid system*				
			A	*B*	*C*	*D*	*E*
Hypersil	90	0.35	0.43	0.67	0.58	–	–
LiChrosorb SI 100	120	0.48	0.72	0.85	–	–	–
LiChrospher SI 100	90	0.44	–	1.24	–	1.12	0.25***
LiChrospher SI 500	18	0.30	–	0.27	–	–	–
LiChrospher SI 1000	11	0.45	–	0.08	–	–	–

* A_s = surface area of silica gel per cm^3 column volume (m^2/cm^3).
** V_p = intra-pore volume per cm^3 column volume (cm^3/cm^3).
*** Reservoir and column at 25°C.

then increases slowly until a constant amount is reached after 150 ml of mobile phase is pumped through. The volume of stationary phase at maximum loading is 0.87 ml, which results in a phase ratio $V_s/V_m = 0.85$. This ratio agrees very well with the one that can be derived from the inter- and intra-pore volumes (*i.e.* 0.84) given in literature[19] when complete pore filling is assumed. However, the volume of mobile phase that must be pumped through to reach a plateau, as well as the final volume of stationary phase, seems to differ significantly with the type of liquid–liquid system, as can be seen from Table I. For instance, with ethyl acetate–water *ca.* 1500 ml must be pumped through to reach a plateau, which then results in a phase ratio of 0.72. Certainly the speed of stationary phase generation is limited by the solubility of the stationary phase in the mobile phase but other factors, especially kinetic factors may be more important, but we could not recognize a clear relationship from the present results. It seems that liquid–liquid systems containing acetate[18] and formate buffers give rise to fast and high stationary phase loading.

Table I shows data on the influence of the support on the phase ratio. As may be expected, apart from the influence of the type of phase system, the surface area and the intra-pore volume play a crucial role in the amount of stationary phase generated. Furthermore, there are indications that small selectivity changes also occur with silica gels from different suppliers. A more detailed study of this phenomenon will be reported in a forthcoming paper. The reproducibility of *in-situ*-generated liquid–liquid systems was investigated by reloading a silica column three times with a ternary liquid system and from the measurement of the capacity ratios of a number of test solutes (Table II). As can be seen from this table, the retention and selectivity are highly reproducible.

Influence of temperature on the phase ratio

The *in situ* coating technique is simple and leads to reproducible and maximum loading of the support with the stationary phase. However, this latter is a disadvan-

TABLE II

REPRODUCIBILITY OF THE CAPACITY RATIO (k') AND SELECTIVITY FACTOR (α) ON AN *IN-SITU*-GENERATED LIQUID–LIQUID SYSTEM

Column support, Hypersil; phase system, B; temperatures: solvent reservoir and column at 22°C.

Compounds (acids)		*Column*					
		I		*II*		*III*	
		k'	α	k'	α	k'	α
1	3-Hydroxycinnamic	1.26	–	1.26	–	1.25	–
2	2,6-Dihydroxybenzoic	2.24	1.78	2.17	1.72	2.21	1.77
3	Hippuric	2.99	1.33	2.88	1.33	2.95	1.33
4	3-Pyridine carboxylic	3.71	1.24	3.63	1.26	3.68	1.25
5	3,4-Diaminobenzoic	4.03	1.09	3.94	1.09	4.00	1.09
6	2-Hydroxy-4-aminobenzoic	5.28	1.31	5.19	1.32	5.25	1.31
7	Benzenesulfonic	7.63	1.45	7.39	1.42	7.52	1.43
8	3,5-Diaminobenzoic	11.52	1.51	11.20	1.51	11.44	1.52
9	4-Aminohippuric	13.89	1.21	13.10	1.17	13.72	1.20

TABLE III

MUTUAL SOLUBILITY OF WATER AND ETHYL ACETATE AT DIFFERENT TEMPERATURES

Temperature (°C)	*Mol fraction of*	
	Ethyl acetate in water	*Water in ethyl acetate*
0	0.0224	0.103
10	0.0200	0.116
20	0.0171	0.130
25	0.0162	0.139
30	0.0155	0.147
40	0.0143	0.167

tage, as it excludes the use of the phase ratio as a parameter for adjusting the degree of retention. In order to create a means of varying the phase ratio in these *in situ*-generated phase systems, the effect of the difference of column and solvent reservoir temperature on the phase ratio and retention was investigated. In these experiments the solvent reservoir temperature was kept constant but the column temperature was raised.

When thermal expansion effects are ignored, the composition of the mobile phase inside the column is similar to that in the reservoir, but at a higher temperature. Owing to the higher temperature of the mobile phase, the solubility of the stationary phase will in most cases be larger and this will result in a decrease of the amount of stationary phase on the support. As an illustration, the mutual solubility of the ethyl acetate–water system at various temperatures is given in Table III. The change of the phase ratio of two liquid–liquid systems with column temperature is given in Fig. 3. As can be seen, the phase ratio decreases rather steeply within the first 2–8°C temperature difference, amounting to a 2- to 4-fold decrease in phase ratio. It must be

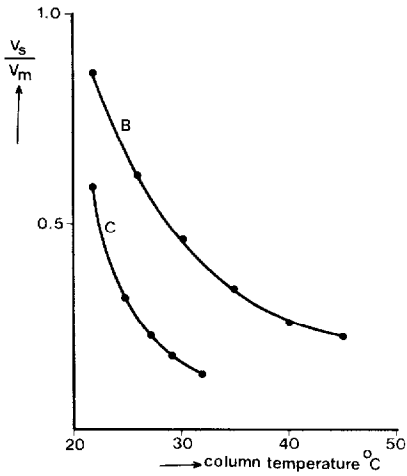


Fig. 3. The phase ratio (V_s/V_m) as a function of the column temperature for a binary and ternary liquid–liquid system. Column supports: system B, LiChrosorb SI 100; system C, Hypersil. Temperatures; reservoir, 22°C; column, 22°C.

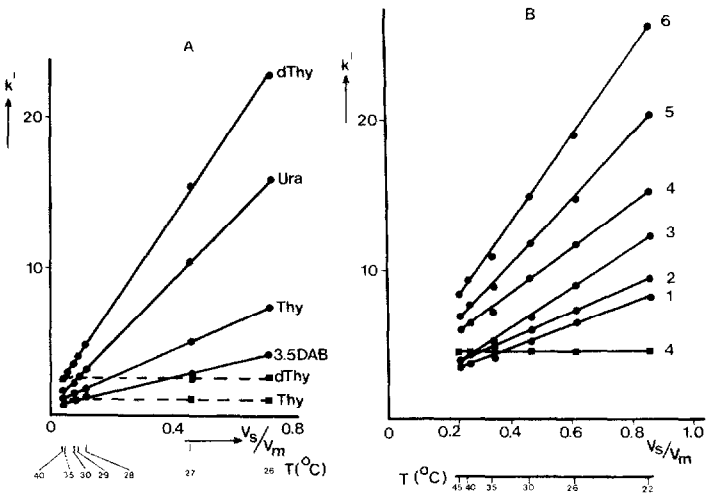


Fig. 4. The capacity ratio (k') of a number of test solutes *versus* the phase ratio at different column temperatures. (A) Phase system A; solvent reservoir, 24°C. Solutes: dThy = thymidine; Ura = uracil; Thy = thymine; 3,5DAB = 3,5-diaminobenzoic acid. (B) Phase system B; solvent reservoir, 22°C. Solutes: 1 = 2,4-dihydroxybenzoic acid; 2 = 2-aminobenzene sulfonic acid; 3 = 3,5-diaminobenzoic acid; 4 = 4-aminohippuric acid; 5 = 2-aminobenzene sulfonic acid; 6 = 4-aminobenzene sulfonic acid. The dashed lines represent k' measurements with a nearly saturated mobile phase.

noted that for some phase systems (not investigated in this study) the mutual solubility of the phases decreases with increasing temperature. In that case, the column temperature must be lower than the reservoir temperature in order to decrease the phase ratio.

Although the composition of the mobile phase will not change significantly with the column temperature, this does not hold for the composition of the generated stationary phase, which must certainly be different from that in the reservoir. The deviation of the composition of the stationary phase in the reservoir from that inside the column depends on the mutual solubility of the liquid phase. For instance, for the ethyl acetate–water system the mutual solubility at various temperatures is known[21] and given in Table III. It shows that the solubility of ethyl acetate in water decreases from 0.017 mol fraction at 20°C to 0.014 at 40°C. This change can hardly influence the nature of the aqueous phase and, thus, the partition coefficients of the solutes. This example demonstrates that for liquid–liquid systems where the mutual solubility of the phases is relatively small, the composition of the stationary phase

TABLE IV

BATCH AND CHROMATOGRAPHICALLY DETERMINED PARTITION COEFFICIENTS (K_p) OF SOME TEST SOLUTES FOR THE ETHYL ACETATE–WATER SYSTEM

	Batch	*Column*
Thymine	8.2	8.5
Uracil	18.6	20.8
Thymidine	25.4	29.6

inside the column is, to a first approximation, independent of the column temperature when the mobile phase composition is kept constant. This assumption is confirmed by Fig. 4, showing the capacity factors of a number of test solutes for two liquid–liquid systems, as measured at various column temperatures. As can be seen, a very good linear relationship is found. The correlation coefficients of the linear regressions were found to be better than 0.9998. In both figures, k' does not go through the origin as it should if liquid–liquid partition is the only distribution process. The occurrence of an intercept must be attributed to residual retention due to adsorption on the support. The contribution of adsorption to the overall retention can be considered as virtually constant over the temperature range investigated, as otherwise the linear behaviour shown in Fig. 4 would not be found. The influence of column temperature of k' of some solutes, measured with a nearly saturated mobile phase (dashed lines in Fig. 4), supports this statement. Note that the residual adsorption in the liquid–liquid systems (the intercept) is about equal to the adsorption, as measured with a nearly saturated mobile phase. Plots such as that shown in Fig. 4 offer the possibility of estimating liquid–liquid partition coefficients, as can be seen if eqn. 1 is rearranged, assuming a constant contribution of adsorption over the investigated temperature range

$$k' = K_{ads} \cdot \frac{A_s}{V_0} + \frac{V_s}{V_m}\left(K_{ads} \cdot \frac{A_s}{V_0} + K_p\right) \tag{2}$$

The liquid–liquid partition coefficient K_p can be calculated from the slope of the correlation of k' *versus* the phase ratio. Table IV shows the partition coefficients of three solutes, as measured batchwise and calculated from Fig. 4 for the ethyl acetate–water system. The agreement is good and shows that variation of the column temperature in order to change the phase ratio could be used for the estimation of partition coefficients. However, this seems to be restricted to binary systems because some preliminary studies on the composition of the stationary phase of ternary phase systems, *e.g.* isooctane–ethanol–water, strongly indicate that the composition of the generated stationary phase differs significantly from that in the reservoir. This is not surprising, as the silica matrix preferentially sorbs the polar components of the phase system.

Practical utility of in-situ-generated liquid–liquid systems

The results obtained so far indicate that liquid–liquid systems can easily be generated on prepacked silica columns. The performance of the silica columns with an average plate number of 9000/15 cm at a linear velocity of 2 mm/s when tested in the adsorption mode, drops to *ca.* 7500/15 cm when used in the liquid–liquid mode. Such a performance is acceptable for most separation problems. The liquid–liquid systems generated seemed to be somewhat sensitive towards changes in room temperature, and this gave rise to noisy baselines at sensitive detector settings. However, this could be easily overcome by operating the column at a temperature 1–2°C higher than that of the reservoir and accepting a somewhat smaller phase ratio.

The applicability of the *in-situ*-generated liquid–liquid systems investigated for the separation of a wide variety of compounds is demonstrated in Figs. 5–8. Fig. 5

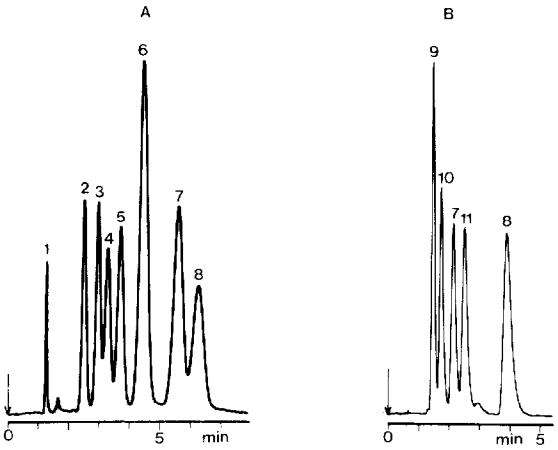


Fig. 5. Separation of test mixtures of steroids in a binary and ternary liquid–liquid system. (A) Column support, LiChrospher SI 100; phase system, E. (B) Column support, Hypersil; phase system, C. Solutes: 1 = butylbenzene; 2 = progesterone; 3 = androstenedione; 4 = testosterone; 5 = 3 β-hydroxy-4-androstene-3,17-dione; 6 = 17α,21-dihydroxy-4-pregnene-3,2-dione; 7 = cortisone; 8 = estriol; 9 = estrone; 10 = estradiol; 11 = hydrocortisone.

shows the separation of some steroids by a binary and ternary phase system. The separation of carboxylic acids of different classes by a chloroform–methanol–formate buffer system is shown in Fig. 6. An efficient and rapid separation of nucleobases and nucleosides can be carried out with the same phase system when the column is operated at a higher temperature, as is demonstrated in Fig. 7. The applicability of an *in-situ*-generated formamide system for the separation of barbiturates is shown in Fig. 8.

The possibility of varying the phase ratio via adjustment of the column temperature offers opportunities for multicolumn operation by applying coupled columns, fed with the same mobile phase but set at different temperatures (which results

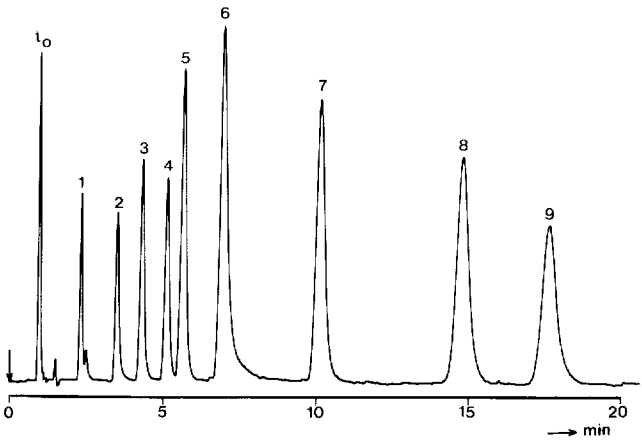
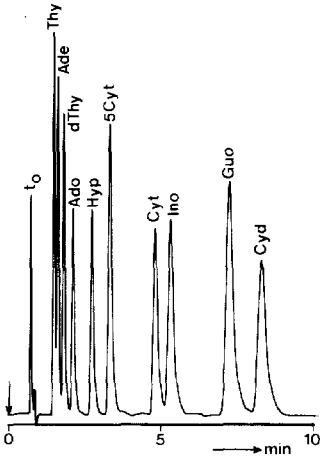


Fig. 6. Separation of a test mixture of acids on a ternary liquid–liquid system. Column support, Hypersil; phase system, B. Solutes: see Table II. Temperatures: solvent reservoir, 22°C; column, 22°C.



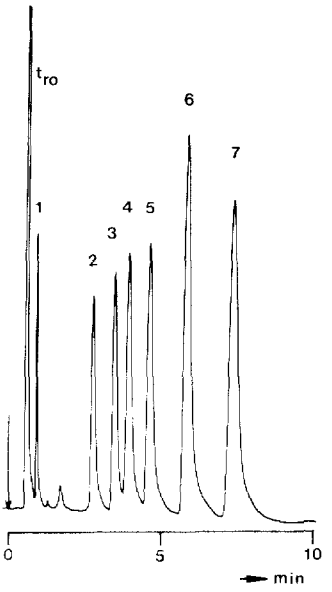


Fig. 7. Separation of nucleobases and nucleosides in a ternary phase system. Column support, Hypersil; phase system, B. Temperatures: solvent reservoir, 22°C; column, 35°C. Solutes: Thy = thymine; Ade = adenine; dThy = thymidine; Ado = adenosine; Hyp = hypoxanthine; 5Cyt = 5-methylcytosine; Cyt = cytosine; Ino = inosine; Guo = guanosine; Cyd = cytidine.

Fig. 8. Separation of a test mixture of barbiturates in an *in-situ*-generated formamide stationary phase. Column support, LiChrosorb SI 100; phase system, D. Temperatures: solvent reservoir, 22°C; column, 22°C. Solutes: 1 = methylphenobarbitural; 2 = amobarbital; 3 = butalbital; 4 = cyclobarbital; 5 = aprobarbital; 6 = allobarbital; 7 = phenobarbital.

in different phase ratios), as demonstrated with aromatic acids in Fig. 9. Of course, similar results can be obtained with two columns, filled with silicas of different surface areas. However, the set-up used in Fig. 9 is more flexible.

CONCLUSIONS

From the results obtained so far, the following conclusions can be drawn. The *in situ* coating technique is applicable to the reproducible generation of stationary phases of various types of liquid–liquid system on prepacked silica columns. The amount of stationary liquid generated and the volume of mobile phase needed to reach equilibrium varies with the nature of the system and depends largely on the surface area of the support. The largest amount of stationary phase generated and the fastest equilibration is found with phase systems containing buffers. Furthermore physical adsorption on the silica matrix contributes to the overall retention of solutes. However, at high stationary phase loading this contribution is usually less than 10% of the total retention.

The phase ratio can be varied over a broad range by adjustment of the temperature difference between the reservoir and the column without significantly influencing the retention characteristics. However, the sensitivity of the phase ratio for

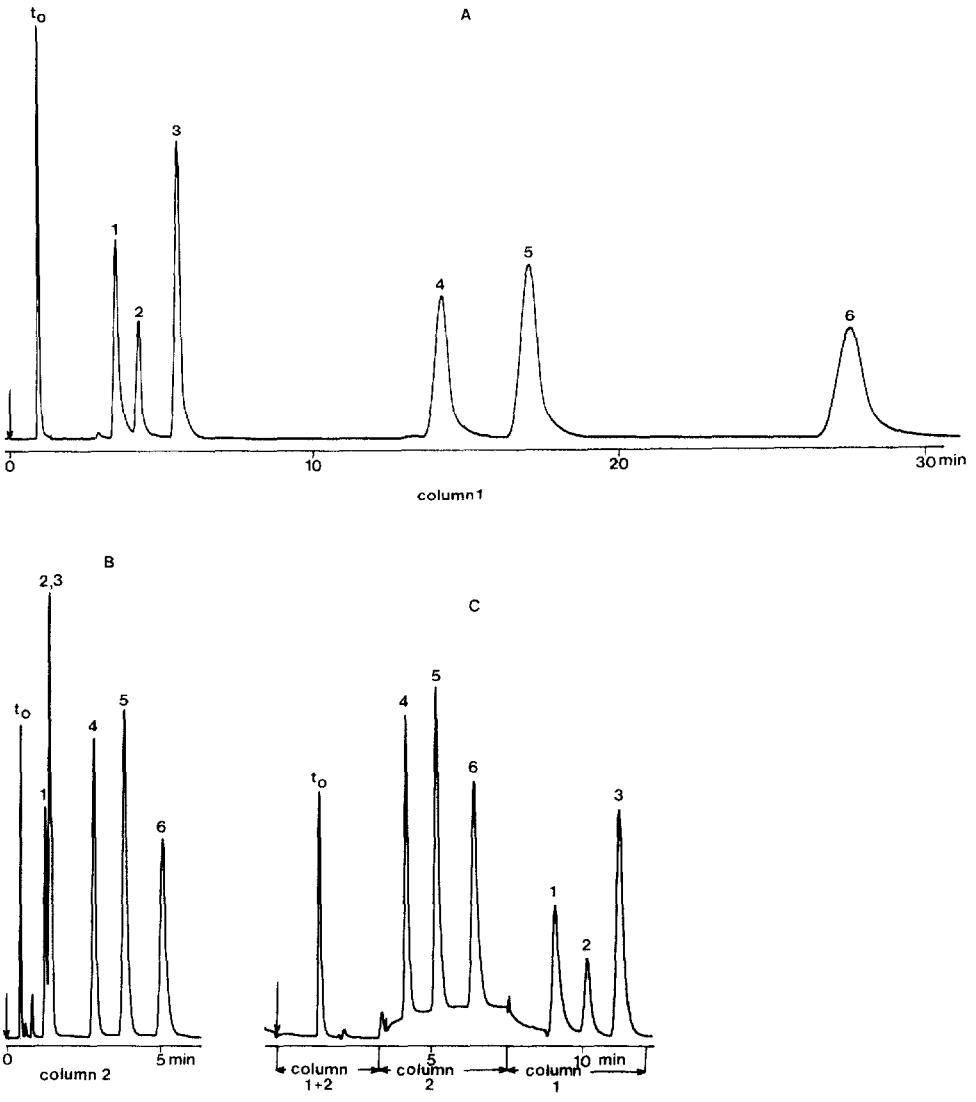


Fig. 9. Illustration of the applicability of the adjustment of the phase ratio via the column temperature in multi-column operation in order to shorten the analysis time. Phase system, B; reservoir temperature, 22°C. (A) Separation of a test mixture of acids on a column kept at 22°C (Column 1). (B) Separation of the same mixture on a column kept at 40°C (Column 2). (C) Separation of the same test mixture when both columns are coupled and column switching is applied.

temperature changes might severely restrict the application of liquid–liquid column chromatography with normal-sized columns to high-speed analysis, because of the radial and axial temperature gradients in the column, caused by frictional heat[21]. The effect of the mobile-phase velocity on the column and retention characteristics associated with the liquid–liquid systems described is now under investigation, and the results will be reported in the next paper.

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REFERENCES

1 J. F. K. Huber, *J. Chromatogr. Sci.*, 9 (1971) 72–76.
2 J. F. K. Huber, J. C. Kraak and H. Veening, *Anal. Chem.*, 44 (1972) 1554–1559.
3 K. Karch, I. Sebastian and I. Halász, *J. Chromatogr.*, 122 (1976) 3–16.
4 C. Gonnet, C. Bory and G. Lachatre, *Chromatographia*, 16 (1982) 243–246.
5 H. Poppe and J. C. Kraak, *J. Chromatogr.*, 255 (1983) 395–414.
6 J. G. Kirchner, in E. S. Perry and A. Weissberger (Editors), *Thin Layer Chromatography, Techniques of Organic Chemistry*, Vol. XII, Interscience Publishers, New York, London, Sydney, 1967.
7 E. Stahl, *Dünnschicht Chromatography*, 2te Auflage, Springer Verlag, Berlin, Heidelberg, New York, 1967.
8 K. Macek and I. Hais, *Stationary Phase in Paper and Thin-Layer Chromatography*, Elsevier, Amsterdam, London, New York, 1967.
9 M. Viricel and M. Lemar, *J. Chromatogr.*, 116 (1976) 343–352.
10 H. Engelhardt and N. Weigand, *Anal. Chem.*, 45 (1973) 1149–1154.
11 J. F. K. Huber, F. F. M. Kolder and J. M. Miller, *Anal. Chem.*, 44 (1972) 105–110.
12 A. F. Hammett, G. E. Pratt, K. M. Scott and R. C. Jennings, in G. E. Pratt and G. T. Brooks (Editors), *Juvenile Hormone Biochemistry*, Elsevier/North Holland, Amsterdam, 1981, pp. 93–105.
13 A. F. Hammett, in C. F. Simpson (Editor), *Techniques in Liquid Chromatography*, Wiley, New York, 1982, Ch. IX.
14 B. A. Persson and B. L. Karger, *J. Chromatogr. Sci.*, 12 (1974) 521.
15 J. Crommen, B. Fransson and G. Schill, *J. Chromatogr.*, 142 (1977) 283.
16 B. Fransson, K.-G. Wahlund, I. M. Johansson and G. Schill, *J. Chromatogr.*, 125 (1976) 327.
17 J. J. Kirkland and C. H. Dilks, Jr., *Anal. Chem.*, 45 (1973) 1778–1781.
18 W. J. Th. Brugman, S. Heemstra and J. C. Kraak, *J. Chromatogr.*, 218 (1981) 285–297.
19 R. Ohmacht and I. Halász, *Chromatographia*, 14 (1981) 155–162.
20 H. Stephen and T. Stephen (Editors), *Solubilities of Inorganic and Organic Compounds*, Vol. I, Part I, Pergamon, Oxford, 1963.
21 H. Poppe, J. C. Kraak, J. F. K. Huber and J. H. M. van den Berg, *Chromatographia*, 14 (1981) 515–523.