Journal of Chromatography, 605 (1992) 167–174
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 323

Solute retention in open-tubular liquid chromatography with flowing retentive liquid

K. Šlais, M. Horká and K. Klepárník

Institute of Analytical Chemistry, Czech Academy of Sciences, Veveří 97, CS-611 42 Brno (Czechoslovakia)

(First received February 11th, 1992; revised manuscript received May 5th, 1992)

ABSTRACT

It is suggested that analytes can be separated in the capillary in which the phase adjacent to the internal surface of the capillary is allowed to flow. The analyte retention in such a capillary is described mathematically and verified on the example of the separation of phenols in the reversed-phase system water–cyclohexanol. Using a capillary of 17 μm I.D., the retentions of hydroquinone and phenol relative to the unretained nitrite ion were 1.95 and 4.4, respectively. The term parallel-current open-tubular liquid chromatography is suggested for this type of capillary separation.

INTRODUCTION

Liquid chromatography (LC), similarly to other chromatographic methods, is usually characterizided as a separation method based on the migration of solutes through a system of two phases in contact, a mobile phase and a stationary phase [1–3]. For chromatographic separation, it is essential that the flow along the separation axis is perpendicular to the process of solute enrichment [4,5]. This means that both phases can move relative to the environment, but each with a different speed and, possibly, in different directions. Counter-current chromatography (CCC) [6] and electrokinetic chromatography (EKC) [7] are examples of the chromatographic modes which also fit such a concept.

Liquid–liquid chromatography (LLC) involves partitioning of the solute between the mobile phase and the liquid stationary phase affixed to a solid support [8]. Until now, LLC has not been widely used because of its inconvenience, mainly due to the need for mobile phase presaturation, system thermostating and equilibration and limited use with gradient elution [1–3]. However, the resolving power, wide applicability, predictable solute retention, high column loadability and relative independence of the column selectivity on the nature of the support are advantages in comparison with other modes of LC.

The potential of open-tubular liquid chromatography was theoretically predicted [4,5,9–11] and many practical obstacles (*e.g.*, detection, sampling, pumping) have been overcome. However, the preparation of a capillary of *ca.* 10 μm I.D. with a stable, reasonable content of the stationary phase is still a problem.

Here we propose carrying out the separation in an open capillary, in which the phase adjacent to the internal surface of the capillary (the retentive phase) is allowed to flow. The retention of a solute in such a capillary is described mathematically. The model function and solute retention were verified experimentally using a capillary of 17 μm I.D. and electrochemical detection of phenolic solutes.

Correspondence to: Dr. K. Šlais, Institute of Analytical Chemistry, Czech Academy of Sciences, Veveří 97, CS-611 42 Brno, Czechoslovakia.

0021-9673/92/$05.00

THEORY

Model description

As the retentive phase is allowed to flow, two practical problems must be solved from the point of view of analytical separations. The retentive phase must be continuously renewed at the beginning of the separation capillary to create a retentive layer on the inner wall, and the retentive phase must not be present as a macroscopically heterogeneous component in the liquid entering the detector placed at the end of separation capillary. Owing to the very minute flows and dimensions involved, the phase separation methods used in the past are not acceptable.

Both of the constraints mentioned can be simply met by exploiting the temperature-dependent solubility of the retentive phase in the mobile phase. The experimental set-up of the chromatograph and its function can be described as follows.

The pump delivers a solution of the retentive phase in the mobile phase via a sampling device. The concentration of retentive phase in the mobile phase, s_1, corresponds to saturation at temperature T_1. This saturated, single-phase solution is pumped at temperature T_1. The separation capillary is maintained at a temperature T_2, which is chosen so that the solubility, s_2, of the retentive phase is lower than that at T_1. Hence, at the beginning of the column, the retentive phase separates from the mobile phase. From the practical point of view, it is advantageous to have T_2 higher than T_1. Then, the column is maintained at a temperature elevated relative to the laboratory temperature.

The internal surface of the capillary is modified so that it is wettable by the retentive phase and thus the internal surface of the capillary is covered by the retentive film. The interfacial force between the retentive and mobile phase together with the frictional force due to flow keeps the thickness of the retentive film constant round the internal circumference of the capillary.

When neglecting the volume contractions, the flow of the retentive phase within the capillary, F_r, is given by the product of the flow-rate of the pumped phase, F_p, and the difference between solubilities s_1 and s_2 expressed in volume fractions:

$$F_r = F_p(s_1 - s_2) \quad (1)$$

The flow of the mobile phase within the capillary, F_m, is then

$$F_m = F_p - F_r = F_p(1 + s_2 - s_1) \quad (2)$$

At the end of the capillary column, both the mobile and retentive phases enter the part of the capillary which is maintained at the temperature at which the solubility of the retentive phase is equal to or higher than that at T_1. As a consequence, the retentive phase dissolves completely prior entering the detector.

Calculation of the solute retention

The average velocity of solute i in equilibrium with g moving phases j can be expressed as

$$u_i = \sum_{j=1}^{g} p_{ji} \langle v_j \rangle \quad (3)$$

where $\langle v_j \rangle$ is the average flow velocity of phase j determined by flow-rate F_j of this phase and its cross-section S_j in which it flows under steady-state conditions:

$$\langle v_j \rangle = F_j/S_j \quad (4)$$

and p_{ji} are the probabilities that particle i is found in phase j, defined to be the fraction of particles i in phase j:

$$p_{ji} = n_{ji} / \sum_{j=1}^{g} n_{ji} \quad (5)$$

where n_{ji} is the number of particles i in phase j.

In the case of two phases, the retentive phase r and the mobile phase m, the respective probabilities can be written in terms of distribution constant $K_i = c_{ri}/c_{mi}$, where c_{ri} and c_{mi} are the concentrations of solute i in the retentive and mobile phase, respectively. Then, it holds for the mobile phase

$$p_{mi} = S_m c_{ri}/(S_m c_{mi} + S_r c_{ri}) = S_m/(S_m + S_r K_i) \quad (6)$$

and analogously for the retentive phase

$$p_{ri} = S_r K_i/(S_m + S_r K_i) \quad (7)$$

where S_r is the cross-section of the retentive layer annuli and S_m the cross-section of the mobile phase cylinder.

Now, after the substitution of eqns. 4, 6 and 7 into eqn. 3, the average velocity u_i of solute i in equilibrium with phases r and m is

$$u_i = (F_m + F_r K_i)/(S_m + S_r K_i) \quad (8)$$

In chromatography, it is usual to express the solute retention by the capacity factor, k_i [1–3], which is related both to the solute retention time, t_{ri}, and to the solute distribution constant, K_i. However, k_i is defined for the immobile stationary phase. Therefore, we use here the term reduced retention, k_i^*, which, similarly to k_i, is defined as the ratio of the solute retention time to the dead time, t_0, minus one: $k_i^* = t_{ri}/t_0 - 1$. The relationship between k_i^* and K_i will be shown below.

From the practical point of view, it is useful to define here the dead time as the migration time of a substance which is not absorbed in the retentive phase and migrates through the column dispersed in the mobile phase only, *i.e.*, at the average velocity $\langle v_m \rangle$. Thus, with respect to eqn. 8, k_i^* for the two-phase flow is

$$k_i^* = \frac{\langle v_m \rangle}{u_i} - 1 = \frac{S_r/S_m - F_r/F_m}{1/K_i + F_r/F_m} \quad (9)$$

where the flow-rate ratio, $F_r/F_m = q$, is given from eqns. 1 and 2 as

$$q = F_r/F_m = \frac{s_1 - s_2}{1 - (s_1 - s_2)} \quad (10)$$

The only quantity that is to be found in eqn. 9 is the ratio of cross-sections of both phases, $\phi = S_r/S_m$. The respective volumes of the retentive and mobile phases in the capillary are determined by the difference in the solubilities $s_1 - s_2$ and by the velocity flow profiles of the two phases. In other words, the flow-rates and viscosities of the phases determine the thickness of the retentive layer, $R - R_c$, and the diameter of the mobile phase cylinder, R_c (see Fig. 1).

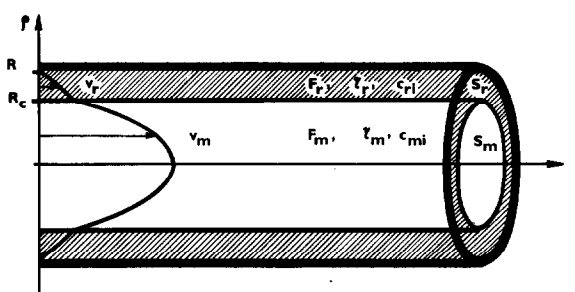

Fig. 1. Flow profiles in open-tubular liquid chromatography with flowing retentive phase. ρ = Radial variable; R = capillary internal radius; R_c = radius of mobile phase cylinder; F_m, F_r = flow-rates of mobile and retentive phase, respectively; η_m, η_r = viscosities of mobile and retentive phase, respectively; c_{mi}, c_{ri} = solute concentrations in mobile and retentive phase, respectively; S_m, S_r = cross-section of mobile and retentive phase, respectively; v_m, v_r = velocities of mobile and retentive phase, respectively, as a function of ρ.

For a two-phase two-dimensional system, the governing differential equations for steady flow velocities are [12]

$$-\frac{\Delta P}{\eta_j L} = \frac{d^2 v_j}{d\rho^2} + \frac{1}{\rho} \cdot \frac{dv_j}{d\rho} \quad j = r, m \quad (11)$$

where η_j is the phase viscosity, ΔP is the pressure drop across the capillary of length L and ρ is the radial distance. This equation gives, after double integration,

$$v_j = \Delta P\, \rho^2/(\eta_j L) + C_j' \ln \rho + C_j'' \quad j = r, m \quad (12)$$

where the integration constants C_j' and C_j'' can be evaluated with the help of the following boundary conditions.

Constant C_m' is zero as v_m does not reach infinity at $\rho = 0$ and because the velocity gradient is zero as a consequence of symmetry:

$$dv_m/d\rho\,|_{\rho=0} = 0 \quad (13)$$

Because of the balance of the friction forces acting at the interface $\rho = R_c$,

$$\eta_r\, dv_r/d\rho\,|_{\rho=R} = \eta_m\, dv_m/d\rho\,|_{\rho=R} \quad (14)$$

constant C_r' is also zero. Constant C_r'' is evaluated with the help of the equality of velocities v_r and v_m at the interface:

$$v_m\,|_{\rho=R_c} = v_r\,|_{\rho=R_c} \quad (15)$$

as $C_r'' = \Delta P\, R^2/(4\eta_r L)$. Zero velocity condition at the inner surface of the capillary,

$$v_r\,|_{\rho=R} = 0 \quad (16)$$

leads to

$$C_m'' = \Delta P/(4L)[R_c^2/\eta_m + (R^2 - R_c^2)/\eta_r]$$

After the substitution of these constants into eqn. 12, the velocity profiles are

$$v_m = \frac{\Delta P}{4L}[(R_c^2 - \rho^2)/\eta_m + (R^2 - R_c^2)/\eta_r] \quad (17)$$

$$v_r = \frac{\Delta P}{4L\eta_r}(R^2 - \rho^2) \quad (18)$$

These equations decribe the velocity profiles of a two-phase flow in a capillary of circular cross-section where the phases create concentric tubes under the action of surface tension. Eqns. 17 and 18 show that the velocity profile of the inner phase is superimposed on the maximum velocity of the outer phase, whereas the profile of the outer phase is unaffected by the inner phase. When $\eta_r = \eta_m$, $R_c = R$ or $R_c = 0$ these equations are transformed into the form of the equation for a one-phase flow.

As stated above, the radius of the mobile phase cylinder R_c is given by the flow-rates of both phases and their velocity profiles. Consequently, R_c can be evaluated by comparing the flow-rate ratio q (eqn. 10) with the ratio of the flow-rates which are obtained by integration of eqns. 17 and 18 over the respective cross-sections. The flow-rates are

$$F_m = \frac{\pi \Delta P}{8\eta_r L}\left(\frac{R_c^4 \eta_r}{\eta_m} - 2R_c^4 + 2R_c^2 R^2\right) \quad (19)$$

$$F_r = \frac{\pi \Delta P}{8\eta_r L}(R_c^2 - R^2)^2 \quad (20)$$

Now, R_c can be found as a solution to the biquadratic equation. The only real and positive root is

$$R_c = R\left(\frac{(q+1) - (q^2 + q\,\eta_r/\eta_m)^{\frac{1}{2}}}{1 - q(\eta_r/\eta_m - 2)}\right)^{\frac{1}{2}} \quad (21)$$

The radius of the mobile phase cylinder is independent of the pumped flow-rate and is controlled only by the physico-chemical parameters of the two phases, *i.e.*, the mutual solubilities at temperatures T_1 and T_2 and viscosities η_r and η_m, respectively.

The phase ratio in the capillary, ϕ, can be expressed as the function of radii R_c and R:

$$\phi = \frac{S_r}{S_m} = \frac{R^2 - R_c^2}{R_c^2} \quad (22)$$

By insertion of eqns. 10 and 21 into eqn. 22 and introducing $t = \eta_r/\eta_m$, and $\Delta s = s_1 - s_2$, we obtain for ϕ

$$\phi = \frac{1 - t + 1/\Delta s}{1/\Delta s - (1 + t(1/\Delta s - 1))^{\frac{1}{2}}} - 1 \quad (23)$$

Based on eqn. 9, the retention of the solute i, expressed in terms of k_i^*, can be calculated by the following equation:

$$k_i^* = (\phi - q)/(1/K_i + q) \quad (24)$$

where the phase ratio, ϕ, is determined by eqn. 23 and the flow ratio, q, is determined by eqn. 10.

EXPERIMENTAL

Capillary preparation

A Simax-type stock glass tube (Kavalier, Sázava, Czechoslovakia) of 7 mm O.D. and 0.6 mm I.D. was drawn using a laboratory-made glass-drawing machine. The capillary obtained, of 0.7 mm O.D. and 17 μm I.D., was hydrophobized by persilylation. The length of the capillary used for chromatographic experiments was 5.670 m.

Chromatograph

The chromatographic system used has been described previously [13]. The pressure source was a VCM 300 micropump (Development Works, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). The sample was injected using a laboratory-made six-port valve with a 20-μl loop and a flow splitter. The splitting ratio was 1:700. The capillary was immersed in a water-bath connected with a U8 thermostat (MLW Prüfgeräte-Werk, Medingen/Sitz Freital, Germany). The capillary was maintained at a constant temperature of 50.0°C. An EMD 10 electrochemical detector (Laboratory Instruments, Prague, Czechoslovakia) was equipped with a thin-layer microcell similar to that described previously [14]. The detector signal was monitored with a TZ 4100 line recorder (Laboratory Instruments).

Mobile phase

The pumped liquid was a 0.1 mol l^{-1} aqueous solution of sodium perchlorate and 1 mmol l^{-1} acetic acid; the solution was saturated with cyclohexanol at 23°C. Based on the interpolation of reported data [15], the difference in the solubilities of cyclohexanol in water between 23 and 50°C was considered to be equal to 0.7 vol.%.

Test solutes

The test solutes were sodium nitrite (dead time marker), gallic acid, 2,5-dihydroxybenzoic acid, hydroquinone, catechol, phenol and 2-nitro-5-aminophenol, purchased from Lachema (Brno, Czechoslovakia).

Viscosity measurement

The viscosities of coexisting liquids in the system cyclohexanol–water at 50°C were measured using a thermostated Ubbelohde viscosimeter. The liquid densities needed were determined pycnometrically. Using reference values for water [16], the densities of the aqueous and organic phases were determined to be 985 and 966 kg m^{-3}, respectively. Further, from ten repetitive measurements, the viscosities η_m and η_r were determined to be 0.57 mN s m^{-2} ± 0.03% and 3.97 mN s m^{-2} ± 0.4%, respectively. Thus, the η_r/η_m ratio was 6.96 at 50.0°C.

Distribution constant determination

The solute K_i was determined by the method described previously [17]. A known amount of analyte was dissolved in the aqueous phase and the absorbance at 288 nm (hydroquinone) or 268 nm (phenol) was determined. The solution was then equilibrated for 2 days at 50°C with a known amount of water-saturated cyclohexanol and the absorbance of the aqueous phase was measured again. The calculated distribution constants for hydroquinone and phenol were 5.0 and 16.7, respectively.

RESULTS AND DISCUSSION

Comparison of theory with experiment

A comparison between the predicted and observed solute retentions can be made from the data summarized in Table I. The values show that the retentions found fit fairly well with the predicted values. Nevertheless, two comments should be made.

Firstly, the ends (about 20 cm in total) of the capillary are maintained at ambient temperature. In this part of the capillary, an appreciable layer of retentive phase should not be present. The negative deviation of the retention from the theory can be up to 3% in the chromatographic configuration used. Second, the calculated retention should be considered as the maximum achievable value. An inhomogeneity in the surface modification can lead to a local decrease in the cross-section of the retentive phase. The role of internal surface modification will be described in detail elsewhere [18].

An example of a chromatogram of phenolic compounds is shown in Fig. 2.

TABLE I

MEASURED AND CALCULATED VALUES FOR REVERSED-PHASE PARALLEL-CURRENT OPEN-TUBULAR LC OF HYDROQUINONE AND PHENOL IN THE SYSTEM WATER–CYCLOHEXANOL

Input values: Δs = 0.007, t = 7.0, $K_{hydroquinone}$ = 5.0, K_{phenol} = 16.7.

Parameter	Hydroquinone	Phenol
q from eqn. 10	0.00705	
ϕ from eqn. 23	0.2293	
k_i^* from eqn. 24	1.072	3.316
k_i^* observed	0.95	3.4
ϕ from eqn. 24 and k_i^* observed	0.204	0.235

Evaluation of the limits of the solute retention

Several interesting features can be concluded from eqn. 24. First, the solute retention is a function only

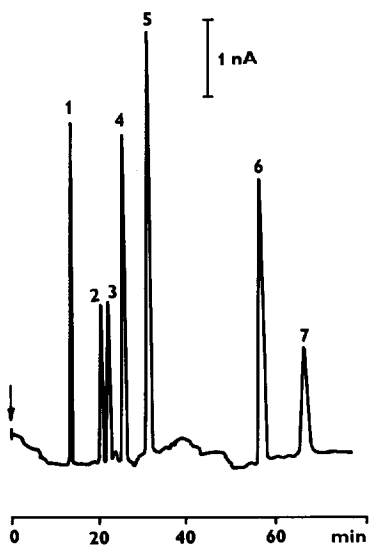

Fig. 2. Chromatogram of separation of phenolic compounds by reversed-phase parallel-current open-tubular liquid chromatography. Capillary: 5.670 m × 17 μm I.D. glass capillary hydrophobized by persilylation; separation temperature, 50°C; mobile phase, 0.1 mol l^{-1} $NaClO_4$–1 mmol l^{-1} acetic acid in water saturated at 23°C with cyclohexanol; detection, amperometric on a platinum electrode; sampling, 20 μl with splitting ratio = 1:700. Peaks: 1 = nitrite ion (dead volume); 2 = gallic acid; 3 = 2,5-dihydroxybenzoic acid; 4 = hydroquinone; 5 = catechol; 6 = phenol; 7 = 2-nitro-5-aminophenol.

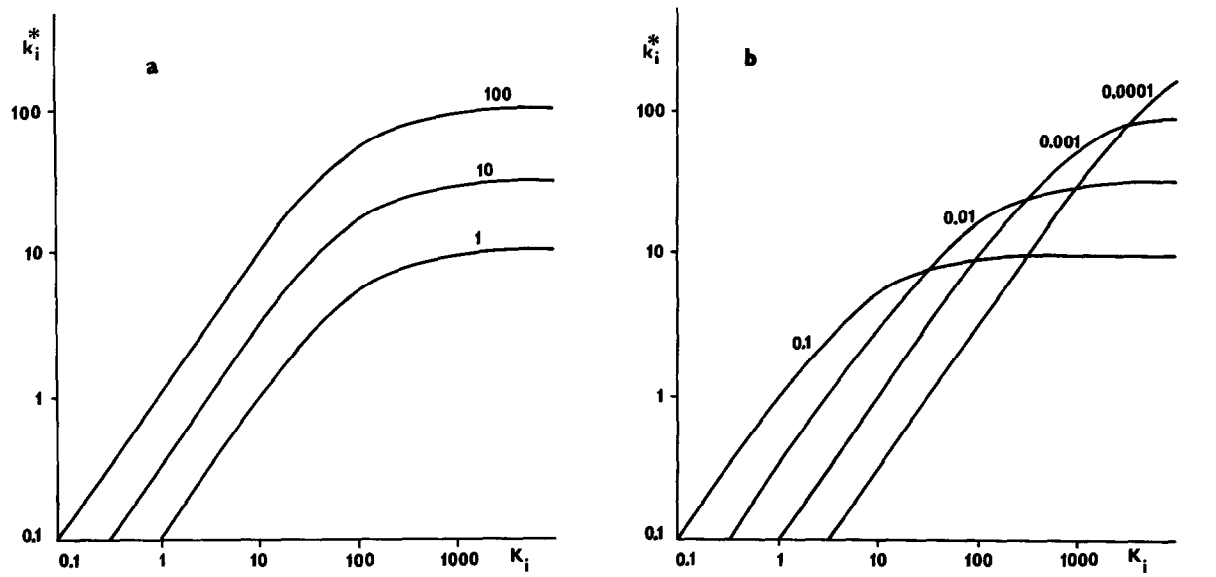

Fig. 3. Plots of dependence of k_i^* on K_i for selected values of Δs and t according to eqn. 24. (a) $\Delta s = 0.01$, t values as shown; (b) $t = 10$, Δs values as shown as a volume fraction of retentive phase in pumped liquid.

of intensive parameters, *i.e.*, temperature, liquid viscosities and component solubilities. No geometrical parameter enters eqn. 24. Hence, as long as eqn. 24 is valid, the capillary dimension can be varied without influencing the solute retention.

It is useful to obtain an idea of the achievable solute retention as a function of Δs, t and K_i. In Fig. 3a, plots of the dependences of k_i^* on K_i for different values of t and a constant $\Delta s = 1\%$ are shown. The examples show that over the whole of the displayed region, an increase in viscosity ratio increases the predicted solute retention. Fig. 3b shows several plots of the dependences of k_i^* on K_i for different values of Δs and a constant $t = 10$. In contrast to Fig. 3a, the influence of the increasing solubility difference is not unambiguous. For low K_i, an increase in Δs predicts a higher k_i^*, whereas for high K_i, the retention should decrease with higher Δs. This can be explained by the retentive phase flow, which increases with increase in Δs (see eqn. 1). To conclude, an increase in retentive phase viscosity is more useful for enhancement of the solute retention than an increase in the difference in retentive phase solubilities between the temperature of the pumped liquid and that of the separation capillary. However, the upper limit of the phase ratio is determined by the retentive film stability. The influence of system parameters on this phenomenon will be discussed elsewhere [18].

If K_i tends to infinity, k_i^* tends to a finite value determined solely by the flow of the retentive phase, F_r. k_i^* of the solute transported exclusively by the retentive phase, $k^*_{i,K\to\infty}$, is

$$k^*_{i,K_i\to\infty} = \phi/q - 1 \qquad (25)$$

This equation corresponds to the tangent of the horizontal part of the graphs for eqn. 24 (see Fig. 3a and b). The practical consequence of this property lies in the self-regenerating ability of the capillary, *i.e.*, every sample component which is soluble in at least one of the liquids within the capillary is sooner or later eluted from the capillary.

For small values of Δs ($\Delta s \ll t$, $\Delta s \ll 1$), eqn. 23 can be simplified to

$$\phi \approx (t\Delta s)^{\frac{1}{2}} \qquad (26)$$

Such a simplified equation can also be derived under the assumption of a linear profile of velocity within the retentive film and the assumption that the mobile phase cross-section is equal to the capillary internal cross-section. The magnitude of the deviation of eqn. 26 from eqn. 23 is shown in Table II for

TABLE II

RATIO OF ϕ VALUES CALCULATED FROM EQN. 23 TO THOSE CALCULATED FROM EQN. 26 FOR SELECTED VALUES OF Δs AND t

Δs (%, v/v)	t			
	1	7	10	100
0.01	1.0101	1.0038	1.0032	1.0011
0.1	1.0326	1.0124	1.0105	1.0036
1.0	1.1111	1.0438	1.0374	1.0152
10.0	1.4625	1.1952	1.1710	1.0898

TABLE III

RATIO OF k_i^* VALUES CALCULATED FROM EQN. 24 TO THOSE CALCULATED FROM EQN. 27 FOR $t = 10$ AND SELECTED VALUES OF Δs AND K_i

Δs (%, v/v)	K_i			
	0.1	1	10	100
0.01	1.00006	0.99996	0.99905	0.99015
0.1	1.0004	0.9995	0.9905	0.9095
1	1.0049	0.9958	0.9136	0.5004
10	1.147	1.0440	0.5495	0.0958

various values of Δs and t. Here, the ratios of the ϕ values calculated from eqn. 23 to the values calculated from eqn. 26 are given. For $\Delta s < 1$ vol.%, the relative difference between eqns. 26 and 23 is below 5%.

For small Δs ($\Delta s \approx q \ll 1/K_i$), eqn. 24 can also be simplified to

$$k_i^* \approx K_i(t\Delta s)^{\frac{1}{2}} \tag{27}$$

Table III gives selected values of k_i^* ratios calculated by dividing eqn. 24 by eqn. 27 and using $t = 10$. For practical values of Δs and t, k_i^* can be estimated from eqn. 27 within a few percent relative error in comparison with eqn. 24.

CONCLUSION

Because, according to the equations derived, the capillary diameter can be varied without influencing the phase ratio, the suggested method is promising for the use of capillaries with even smaller diameter than used here. Evaluation of the upper limit of the phase ratio in relation to the retentive film stability needs further study.

The temperature dependence of the phase ratio evokes the idea of simple control of solute retention by choice of the capillary temperature. Even more, the temperature programming should be an efficient tool for retention control during the chromatographic separation.

More basically than other liquid–liquid chromatographic methods, the approach presented here substantially reduces problems connected with the interaction of the analyte with solid sorbents, supports or other solid matrices. In comparison with other separation methods that are based on a perpendicular arrangement of liquid flow displacement and relative displacement, and that do not need any solid matrix (*e.g.*, countercurrent chromatography, field-flow fractionation [4,5]) the suggested method offers a much higher number of theoretical plates generated per unit time. In comparison with the modes of open-tubular liquid–liquid chromatography presented up to now, the suggested method simplifies substantially the capillary preparation, which makes open-tubular LC more attractive for the solution of practical analytical problems.

The term parallel-current open-tubular liquid chromatography is suggested for the method presented.

In the near future, the influence of the physical properties of the solvent, modification of the capillary internal surface and the mobile phase velocity will be studied from the point of view of optimization of the performance of the method.

REFERENCES

1 B. L. Karger, L. R. Snyder and Cs. Horváth, *An Introduction to Separation Science*, Wiley, New York, 1973.
2 Z. Deyl, K. Macek and J. Janák, *Liquid Column Chromatography*, Elsevier, Amsterdam, 1975.
3 L. R. Snyder and J. J. Kirkland, *Introduction to Modern Liquid Chromatography*, Wiley, New York, 1979.
4 J. C. Giddings, *Anal. Chem.*, 53 (1981) 945A.
5 J. C. Giddings, *J. Chromatogr.*, 395 (1987) 19.
6 N. B. Mandava and Y. Ito (Editors), *Countercurrent Chromatography*, Marcel Dekker, New York, 1988.
7 S. Terabe, *Trends Anal. Chem.*, 8 (1989) 129.

8 A. J. P. Martin and R. L. M. Synge, *Biochem J.*, 35 (1941) 1358.
9 J. H. Knox and M. T. Gilbert, *J. Chromatogr.*, 186 (1979) 405.
10 J. H. Knox, *J. Chromatogr. Sci.*, 18 (1980) 453.
11 J. W. Jorgenson and E. J. Guthrie, *J. Chromatogr.*, 255 (1983) 355.
12 R. B. Bird, W. E. Stewart and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1965.
13 K. Janák, M. Horká and M. Krejčí, *J. Microcol. Sep.*, 3 (1991) 203.
14 K. Šlais and M. Krejčí, *J. Chromatogr.*, 235 (1982) 21.
15 R. Stephenson and J. Stuart, *J. Chem. Eng. Data*, 31 (1986) 56.
16 R. C. Weast (Editor), *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 68th ed., 1987–88.
17 J. F. K. Huber, C. A. M. Meijers and J. A. R. J. Hulsman, *Anal. Chem.*, 44 (1972) 111.
18 K. Šlais and M. Horká, in preparation.