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Note

Comparison of high-performance liquid chromatographic and thin-layer chromatographic data obtained with various types of silica

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An important aim of the optimization of chromatographic systems is to establish a suitable range of capacity ratios of the solutes to be separated. For mixtures consisting of few components, typical ranges are 1–10 for column chromatography and 0.1–5 for flat-bed techniques. Instead of a long series of solvents proposed for earlier eluotropic series, binary mixtures of several solvents can be used[1–3]; the elution strength can then be finely adjusted to the required value by choosing the composition of the mixture. The choice of solvents of suitable strengths and selectivities for column separations can be conveniently carried out by the thin-layer technique[4–7].

In a preceding paper[6], the capacity ratios of several solutes were compared for analogous systems in column and thin-layer chromatography. To ensure that optimal comparisons could be made, the same adsorbent was used in both series of experiments. As the adsorbents used in high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC) often have different properties, in this several types of silica were used in the TLC experiments.

EXPERIMENTAL

Column chromatography was carried out using a DuPont Model 830 liquid chromatograph with a UV detector. A steel column (50 cm × 2.1 mm I.D.) was packed with silica SI 60 (Merck, Darmstadt, G.F.R.) obtained by sedimentation of silica gel G for TLC. TLC experiments were carried out using glass plates (18 × 20 cm) covered with silica of four types: silica gel G after Stahl and Kieselgel 60 HR (Merck, G.F.R.), silica gel for TLC (Woelm, Eschwege, G.F.R.) and wide-pore silica (Polish Reagents, Gliwice, Poland), milled and graded by sedimentation.

Solutions of ethyl acetate in cyclohexane were used as the mobile phase. The details of the column and TLC experiments have been given earlier[6].

RESULTS AND DISCUSSION

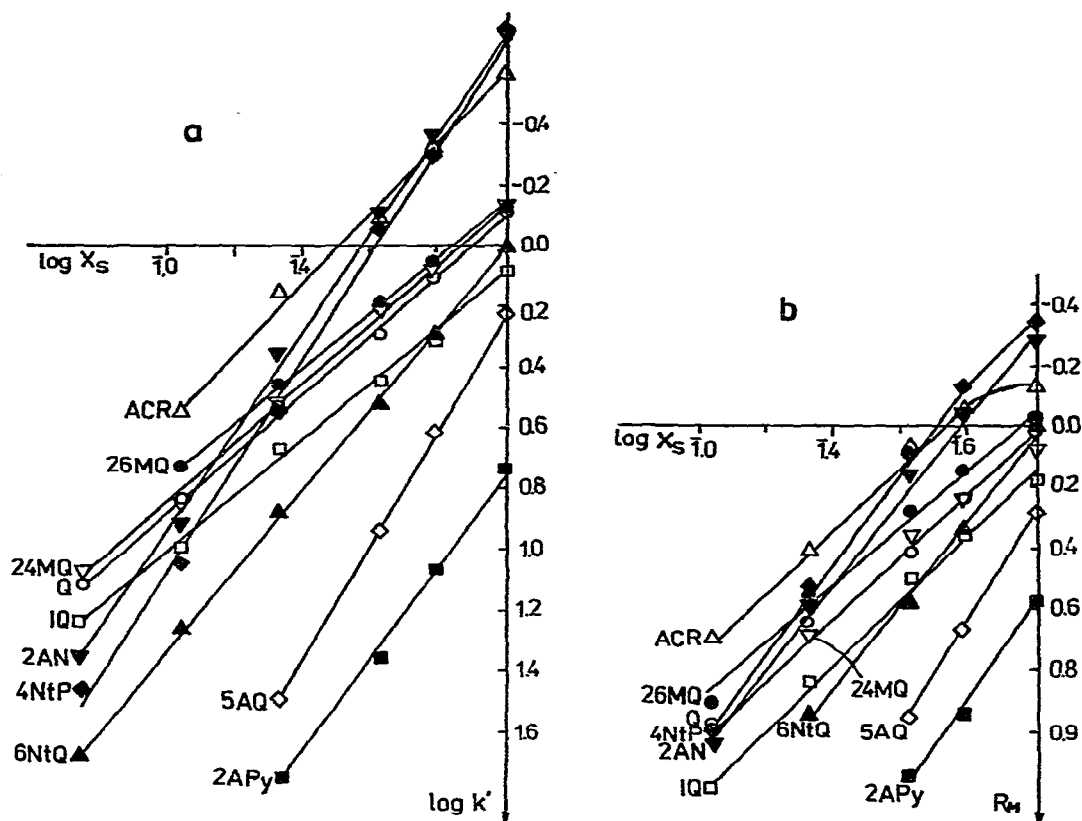In the first series of experiments, relationships between capacity ratios and

Fig. 1. log k' *versus* log mole-% ethyl acetate plots obtained for (a) column chromatography, $k' = (t_R - t_R^0)/t_R^0$, and (b) TLC, log $k' = R_M$. Abbreviations of solutes as in Table I.

TABLE I

SLOPES (ABSOLUTE VALUES) OF GRAPHS OF LOG k' *versus* LOG MOLE FRACTION OF ETHYL ACETATE

Solute	Abbreviation	Column data	TLC data		
			Silica gel G after Stahl	Kieselgel 60 HR	Woelm silica gel
Quinoline	Q	1.0	1.0	0.7	1.1
Isoquinoline	IQ	0.9	1.1	0.9	1.2
Acridine	ACR	1.2	1.1	0.9	1.0
5-Aminoquinoline	5AQ	1.9	1.8	1.4	1.6
2,4-Dimethylquinoline	24MQ	1.0	1.0	0.8	1.1
2,6-Dimethylquinoline	26MQ	0.9	1.0	0.8	1.0
6-Nitroquinoline	6NtQ	1.3	1.4	1.0	1.4
2-Aminopyridine	2APy	1.5	1.6	1.1	1.5
4-Nitrophenol	4NtP	1.7	1.5	1.2	1.4
2-Aminonaphthalene	2AN	1.6	1.4	1.2	1.3

solvent composition were determined in order to find the optimal composition of the developing solvent. The relationships, plotted on a logarithmic scale, were linear, in accordance with adsorption models based on the law of mass action applied to the competitive adsorption of solute and solvent molecules[8–11], their slopes probably being related to the molecular mechanism of adsorption[9–12]. The slopes and relative positions of log k' versus log [EtOAc] lines obtained by the two techniques were generally in good agreement (Fig. 1; Table I), although the slopes for TLC on Kieselgel 60 HR were lower. As the R_F values of most solutes in the TLC experiments were mostly below 0.50, the R_M values were calculated without correction for gradient effects ($\xi = 1.0$).

It follows from Fig. 1 that a suitable range of k' values is obtained for a concentration of ethyl acetate in the developing solvent of 60%. TLC experiments were therefore repeated using silica gels of different types in strictly parallel runs. The R_F values determined were means from three runs, and were reproducible to within ±0.02 unit. The graphical correlations of column and thin-layer chromatography data are presented in Figs. 2 and 3. At first, the R_M values for log k' versus log k'_{TLC} correlations were calculated without correction for gradient effects ($\xi = 1.0$; Fig. 2a). However, it was noticed in other experiments, especially with mobile phases containing polar solvents with small molecules (methanol, acetone, ethyl acetate) that even weakly adsorbed solutes did not reach the limiting value of $R_F = 1$. This result indicated that gradient effects should be taken into account and, as the limiting value was ca. 0.8, in further correlations the R_M values were taken from tables in which the correction factor $\xi = 1.2$ was used[4,13]. This correction resulted in less steep correlation lines, the
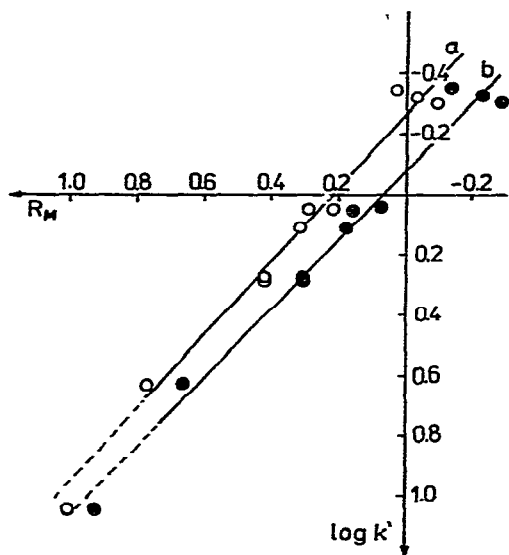

Fig. 2. log k' versus R_M correlations. Silica gel G after Stahl was used in both techniques. (a) $\xi = 1.0$; (b) $\xi = 1.2$.
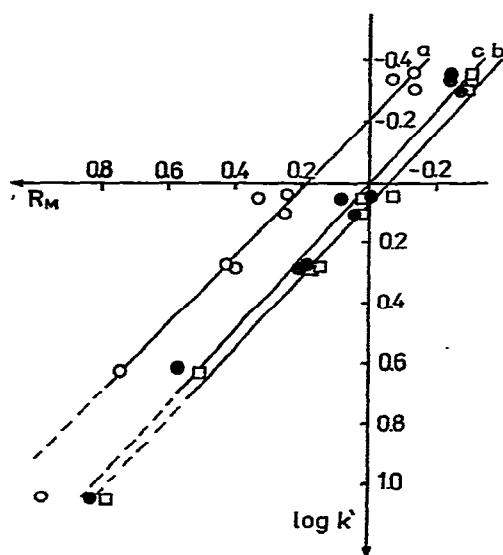
Fig. 3. log k' versus R_M correlations. Silica gel G after Stahl used in column experiments and (a) Kieselgel 60 HR, (b) Woelm silica gel and (c) Polish Reagents silica were used in TLC; $\xi = 1.2$. The straight lines were calculated by the method of least squares.

slopes of which were closer to the theoretical value of unity (Figs. 2b and 3). For instance, the correlation lines in Fig. 2 calculated by the method of least squares (neglecting the lowest point whose coordinates are less accurate) are

$$\log k' = 1.23\, R_M - 0.29 \qquad \text{(Fig. 2a; } \xi = 1.0)$$
$$\log k' = 1.14\, R_M - 0.08 \qquad \text{(Fig. 2b; } \xi = 1.2)$$

Both correlations are satisfactory as far as the optimization of $\log k'$ values are concerned; however, the data seem to indicate that even higher correction factors (e.g., 1.4) could be necessary, at least for some adsorbents and solvents, in order to attain the theoretical slope of unity for $\log k'$ versus R_M correlations.

In Fig. 3, the R_M values obtained for the remaining silicas are plotted against column data obtained for the silica SI 60. The correlations are satisfactory, confirming the usefulness of TLC as a reconnaissance technique for column experiments. The equations of the correlation lines in Fig. 3 ($\xi = 1.2$) are as follows:

Fig. 3a: $\log k' = 1.13\, R_M - 0.21$ (Kieselgel 60 HR)
Fig. 3b: $\log k' = 1.19\, R_M + 0.07$ (Woelm silica gel)
Fig. 3c: $\log k' = 1.22\, R_M + 0.01$ (Polish Reagents silica)

The vertical positions of the lines depend on the ratios of adsorbent weight to solvent volume in the two techniques (cf., the coefficient k_f in ref. 4) and the ratio of specific surface areas if different adsorbents are used in column and TLC experiments, and can also be influenced by open-bed effects, which require the use of the correction coefficients (ξ). They also depend on the activity of the adsorbents[4,5]; however, standardization of the experimental conditions, especially the use of saturated tanks and pre-conditioning of the plates before development, results in satisfactory predictions of column parameters from TLC data, even for different adsorbents of the same general type and for different compositions of the mobile phase[6]. It should be pointed out, however, that the investigations were concerned with systems of the type polar sample–polar solvent–wide pore silica.

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