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TWO-COMPONENT SOLVENT SYSTEMS IN ADSORPTION CHROMATOGRAPHY ON SILICA GELS WITH DIFFERENT SPECIFIC SURFACE AREAS*

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SUMMARY

In adsorption flat-bed and column liquid chromatography, multicomponent solutions are most frequently used as mobile phases as they enable the range of combinations of chromatographic systems to be increased. Flat-bed chromatography frequently gives a preliminary determination of the optimal conditions for the chromatographic separation of mixtures in liquid column and high-efficiency chromatography. Therefore, the development of the possibilities of separating a mixture of substances on the basis of the data for the adsorption of the pure components on solid adsorbents is very important.

The relationship between theoretical and experimental $R_{M_{1,2}}$ values and the composition of the conformal system carbon tetrachloride–chloroform used as the mobile phase was studied, using silica gels with different specific surface areas as adsorbent. The results showed good agreement between theoretical functions $R_{M_{1,2}} = f(\varphi_1)$ and the experimental functions, where φ_1 is the volume fraction of component 1 in the mobile phase. It was found that the value of a particular function depended on the specific surface area of the adsorbent. Some deviations from the observed regularities were found to be caused by the large interaction energies of the adsorbents with large specific surface areas on the separated substances and molecules of the mobile phase.

INTRODUCTION

At the present stage of development of chromatographic separations, different single-component and multicomponent liquid phases are in use and there are therefore many possible combinations of mixtures which can give rise to serious problems in selecting the optimal chromatographic system. Because of the limitations of separa-

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tions with a single-component mobile phase, multicomponent mobile phases are frequently used in adsorption liquid chromatography because they permit a greater differentiation of the separated substance–solvent–adsorbent interactions that govern the efficiency of the separation a mixture.

A separation by either conventional or high-efficiency column chromatography is preceded by a study of similar systems by flat-bed chromatography, which permits a simple and rapid selection of suitable separation systems and prevents wastage of often expensive mobile phases. These preliminary investigations of chromatographic systems by flat-bed chromatography have even greater importance in the case of some preparative separations of mixtures by conventional or high-efficiency liquid column chromatography. Therefore, theoretical investigations of methods for the prediction of chromatographic separations of mixtures are very important.

Methods for the selection of the optimal mobile phases in flat-bed, liquid and column chromatography may be aided by investigations of the adsorption of multicomponent solvents, the results of which may, with some modifications, be used in adsorption liquid chromatography.

THEORETICAL

Theoretical studies by Ościk[1,2] on adsorption from multicomponent solvents permit an equation to be obtained that relates the R_M value of a substance in a mixed solvent ($R_{M_{1,2}}$) and the R_M values of the substance in pure solvents 1 and 2 to the adsorption data on solid adsorbents:

$$R_{M_{1,2}} = \varphi_1 \Delta R_{M_{1,2}} + (\varphi_1^s - \varphi_1)(\Delta R_{M_{1,2}} + A_z) + R_{M_2} \tag{1}$$

where

$$R_M = \log\left(\frac{1 - R_F}{R_F}\right) \tag{1a}$$

according to Bate-Smith and Westall[11] $R_{M_{1,2}}$ is the R_M value of a substance z using the two-component solvent 1 + 2, R_{M_1} and R_{M_2} are the R_M values of substance z in pure solvents 1 and 2, respectively

$$\Delta R_{M_{1,2}} = R_{M_1} - R_{M_2}$$

φ_1 is the volume fraction of component 1 in the mobile phase, φ_1^s is the volume fraction of component 1 in the surface phase, where

$$\varphi_1^s = \frac{\varphi_1 K_1}{1 + (K_1 - 1)\varphi_1} \tag{2}$$

and it was assumed that

$$K_1 = -\log \Delta R_{M_{1,2}}$$

and $A_z = \log k_{1,2}^{\infty}$, where $k_{1,2}^{\infty}$ is a hypothetic rational partition coefficient of substance z between components 1 and 2.

The difference $\varphi_1^s - \varphi_1$ expresses the adsorption of the components of the two-component mobile phase, if its composition is given. This difference can be estimated on the basis of the adsorption isotherm of the components of mobile phase. $k_{1,2}^{\infty}$ represents molecular interactions between molecules of substance z and solvent molecules.

Previous work[1-4] showed that the theoretical functions $R_{M_{1,2}} = f(\varphi_1)$ for ideal two-component solvents as the mobile phase have similar shapes to the same functions obtained experimentally. Even approximate qualitative adjustment of the experimental curves to theoretical functions $R_{M_{1,2}} = f(\varphi_1)$ results in close similarity. The correctness of the equation in question was also checked by an experimental method[4].

The agreement of the experimentally obtained relationships $R_{M_{1,2}} = f(\varphi_1)$ with those calculated theoretically will depend on a series of parameters relating to adsorption from multicomponent solvents, *viz.*, type of mobile phase, type of adsorbent and structure of the substance being chromatographed.

The aim of the present work was the examination of a correlation between the experimental and theoretical relationships $R_{M_{1,2}} = f(\varphi_1)$ for the case of a two-component mobile phase, taking into consideration different types of adsorbents and of substances being chromatographed.

EXPERIMENTAL

Experimental relationships $R_{M_{1,2}} = f(\varphi_1)$ of the substance were obtained by measurements of R_F values by ascending adsorption thin-layer chromatography. Silica gels with different microporous structures (Table I) were used as adsorbents as 0.3-mm layers on plates. The adsorbents were activated for 2 h at 135°.

TABLE I

ADSORBENTS USED

Particle diameter of the adsorbents = 0.08–0.10 mm.

Adsorbent	*Amount of water for preparing sorbent suspension (ml per 25 g)*	*Specific surface area, B.E.T.* (water vapour) (m²/g)*	*Average radii of capillaries (Å)*
Silica gel A	38	565	10
Silica gel B	39	337	10
Silica gel D	59	122	8
Silica gel E	59	58	7

* Brunauer, Emmett and Teller[12] equation.

Substances that belong to various classes according to the Pimentel and McClellan classification[5] were used as model substances: *o*-nitrophenol (class AB), 1-naphthol (class AB), 8-methylquinoline (class B) and carbazole (Class AB). The chromatograms were developed for a distance of 16 cm and detection was carried out by using Dragendorff reagent or UV light[6]. The mobile phase was the two-component conformal solvent system carbon tetrachloride–chloroform (class N + A) so that the effects of the mobile phase were practically eliminated. All measurements

TABLE II

EXPERIMENTAL R_F VALUES OF *o*-NITROPHENOL, 1-NAPHTHOL, 8-METHYLQUINOLINE AND CARBAZOLE OBTAINED BY ADSORPTION TLC ON ADSORBENTS WITH DIFFERENT SPECIFIC SURFACE AREA

Mobile phase: carbon tetrachloride–chloroform in various proportions.

Adsorbent	*Substance*	R_F						
		Pure CCl_4	*Pure* $CHCl_3$	CCl_4–$CHCl_3$ *solution composition (volume fraction of* $CHCl_3$*)*				
				0.1	*0.3*	*0.5*	*0.7*	*0.9*
Silica gel A	*o*-Nitrophenol	0.15	0.69	0.33	0.53	0.61	0.67	0.67
	1-Naphthol	0.01	0.22	0.06	0.15	0.18	0.24	0.24
	8-Methylquinoline	0.02	0.08	0.05	0.11	0.20	—	0.20
	Carbazole	0.07	0.53	0.14	0.33	0.50	—	0.64
Silica gel B	*o*-Nitrophenol	0.18	0.53	0.24	0.36	0.47	0.53	0.53
	1-Naphthol	0.01	0.18	0.05	0.14	0.15	0.18	0.18
	8-Methylquinoline	0.02	0.08	0.05	0.14	0.17	0.20	0.15
	Carbazole	0.07	0.53	0.14	0.29	0.39	0.44	0.50
Silica gel D	*o*-Nitrophenol	0.31	0.78	0.39	0.50	0.59	0.69	0.74
	1-Naphthol	0.09	0.52	0.12	0.20	0.29	0.39	0.47
	8-Methylquinoline	0.11	0.53	0.17	0.24	0.33	0.42	0.50
	Carbazole	0.24	0.69	0.13	0.47	0.51	0.61	0.33
Silica gel E	*o*-Nitrophenol	0.31	0.50	0.36	0.53	0.51	0.51	0.52
	1-Naphthol	0.08	0.39	0.09	0.20	0.33	0.39	0.39
	8-Methylquinoline	0.03	0.53	0.11	0.31	0.39	0.42	0.44
	Carbazole	0.15	0.67	0.26	0.44	0.53	0.58	0.61

were made at about 24° by a standard method[7–9], and the R_F values are given in Table II. R_M values were evaluated according to eqn. 1a.

The results of the measurements were expressed as graphs of the relationship $R_{M_{1,2}} = f(\varphi_1)$, with experimental $R_{M_{1,2}}$ values as points on the graphs. Theoretical functions $R_{M_{1,2}} = f(\varphi_1)$ for individual substances were calculated from eqn. 1. By choosing a K_1 value for a given mobile phase, an average $\Delta R_{M_{1,2}}$ value of the substance being chromatographed can be considered to be approximately equal to $-\log K_1$. Suitable values of $A_z = \log k^{\infty}_{1,2}$ were chosen[3].

RESULTS AND DISCUSSION

Correlations between the relationships $R_{M_{1,2}} = f(\varphi_1)$ obtained experimentally and calculated theoretically on the basis of eqn. 1 for some aromatic compounds are presented in Figs. 1 and 2. Good agreement for both of these relationships was obtained by using carbon tetrachloride–chloroform as the mobile phase.

Fig. 1 gives results for *o*-nitrophenol and 1-naphthol, and shows that the highest R_M values of each substance are obtained on adsorbents with large specific surface areas (565 m^2/g). The R_M values of the substances decreased in stationary phases with smaller specific surface areas. For both substances, good agreement between the theoretical and experimental relationships $R_{M_{1,2}} = f(\varphi_1)$ was observed, indicating that eqn. 3 describes correctly the chromatographic process of the mixture of sub-

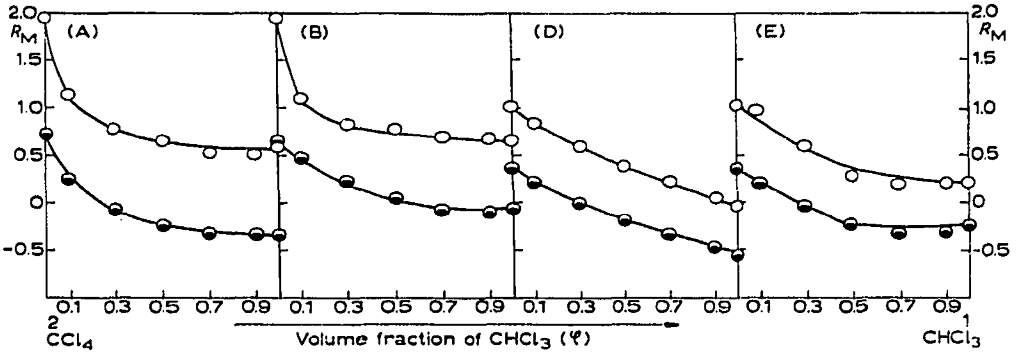

Fig. 1. Comparison of theoretical (line) and experimental (points) values of the functions $R_{M_{1,2}} = f(\varphi_1)$ for o-nitrophenol (◒) and 1-naphthol (○) obtained by using carbon tetrachloride–chloroform as the mobile phase. A, B, D and E indicate the type of silica gel adsorbent used. Specific surface area (m^2/g): A, 565; B, 337; D, 122; E, 58.

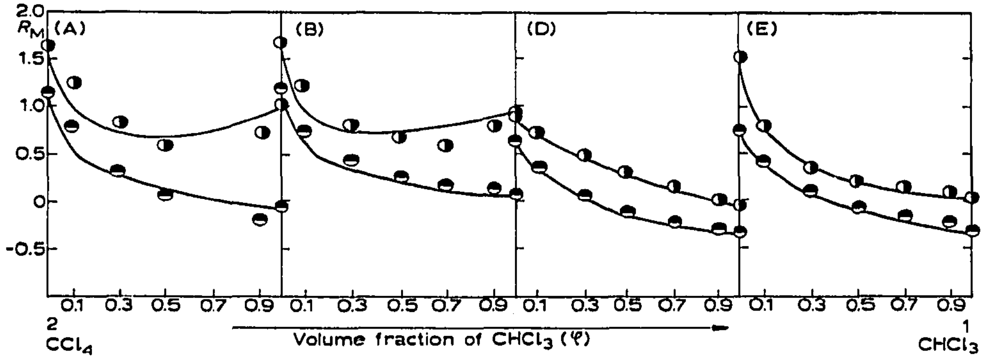

Fig. 2. Comparison of theoretical and experimental relationships $R_{M_{1,2}} = f(\varphi_1)$ for 8-methylquinoline (◑) and carbazole (◒). For details, see Fig. 1.

stances examined in carbon tetrachloride–chloroform over the whole range of concentrations.

Fig. 2 shows the theoretical and experimental relationships $R_{M_{1,2}} = f(\varphi_1)$ obtained for 8-methylquinoline and carbazole, and shows agreement between these relationships. However, on adsorbents with large specific surface areas (Fig. 2A and B) there were some differences between the theoretical and experimental relationships, which possibly result from interactions of the adsorbent or mutual interactions between the molecules of solvents 1 and 2 and the molecules of the substance being chromatographed. This necessitates the use of the complementing theoretical eqn. 1 when highly active adsorbents are used. Good agreement between the theoretical and experimental relationships are shown in Fig. 2D and E for adsorbents with smaller specific surface areas.

These results show that the equation used in this paper characterizes well the chromatographic process in adsorption TLC when two-component conformal mobile phases are used. In general, the equation can be safely applied when using adsorbents with different microporous structures.

Figs. 1 and 2 show that the $\Delta R_{M_{1,2}}$ values of the substances or $-\log K_1$ are

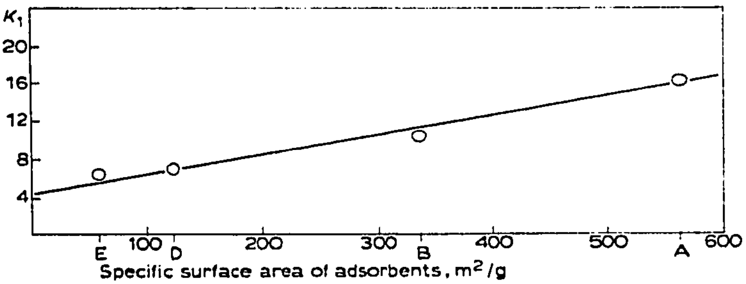

Fig. 3. K_1 as a function of the specific surface area of the adsorbent.

closely related to the microporous structure of the adsorbent. The relationship is shown in Fig. 3, where it can be seen that the relationship $K_1 = f(s)$ is linear. On adsorbents with large specific surface areas, K_1 has high values, and *vice versa*, as a result of increased adsorption of component 1 in the solution of 1 + 2. A more detailed examination of K_1 will possibly allow more general conclusions to be reached, thus permitting a more comprehensive characterization of the chromatographic process in adsorption thin-layer and liquid chromatography. This will help to characterize the properties of adsorbents by using the simple chromatographic method. These aspects are under investigation and will be published elsewhere[10].

The above considerations may also possibly apply under the conditions of liquid column chromatography.

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