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## COMPARISON OF THEORETICAL AND EXPERIMENTAL $R_{M}$ VALUES IN THIN-LAYER ADSORPTION CHROMATOGRAPHY ON SILICA GEL ADSORBENTS OF DIFFERENT POROSITY

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### SUMMARY

The agreement between theoretical and experimental  $R_{M_{1,2}}$  values obtained for some aromatic compounds by thin-layer adsorption chromatography has been examined in relation to the pore diameter (60–1000 Å) of the silica gel adsorbents used. The greatest changes in the parameters considered take place when the pore diameter does not exceed 200 Å, above this value the changes are slight. Fairly good agreement between values calculated from the theoretical relation  $R_{M_{1,2}} = f(\varphi_1)$  and experimental  $R_{M_{1,2}}$  values has been obtained for all of the adsorbents examined.

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### INTRODUCTION

Mathematical models which take into account the properties of chromatographic systems are useful in predicting optimum separation conditions<sup>1-10</sup>. Theoretical relations for mixed-solvent systems give best agreement with experimental results if the solvents form ideal solutions, *i.e.*, those without selective molecular interactions<sup>5,6,11-14</sup>, otherwise complications may occur<sup>4,8,15</sup>. Ościk<sup>4,5,16-18</sup> derived such a relation based on the thermodynamic theory of adsorption:

$$R_{M_{1,2}} = \varphi_1 \Delta R_{M_{1,2}} + (\varphi_1^s - \varphi_1) (\Delta R_{M_{1,2}} + A_2) + R_{M_2} + Y \quad (1)$$

The definition and method of calculation of the quantities in eqn. 1 can be found in the preceding<sup>19</sup> and earlier<sup>5,11,12,14</sup> papers. The equation has been found to be applicable even for non-ideal (interacting) solvent systems.

Many papers stress the role of the adsorbent in thin-layer adsorption chromatography (TLAC)<sup>3,11-15,20-22</sup>. The porosity of the adsorbent is among the factors which affect its interaction with solutes and solvents and thus the chromatographic mobility of compounds.

## EXPERIMENTAL

Experimental  $R_F$  values (Table I) obtained by TLAC served as a basis for calculating  $R_M$  values on four silica gel adsorbents of a different pore diameter (E. Merck, Darmstadt, G.F.R.). The mobile phase was carbon tetrachloride-chloroform (N + A)<sup>23</sup>. The lack of hydrogen-bond interactions is a characteristic of this system. The compounds investigated were 1-naphthol and 2-naphthol (class AB, according to the classification of Pimentel and McClellan<sup>23</sup>), quinoline (class B), 8-hydroxyquinoline (class AB), 8-methylquinoline (class B), fluorenone (class B) and carbazole (class AB). The chromatographic process was carried out by the ascending technique as described previously<sup>11,12,24,25</sup>. The spots were detected with ultraviolet (UV) light or with iodine vapour.

The results of the measurements are given as graphs of the theoretical relation  $R_{M1,2} = f(\varphi_1)$  calculated from eqn. 1 (solid and broken lines) and as the experimental points.

Values of  $K_i^{11-15}$ , which are characteristics of the adsorption of the components of the mobile phase and are required for finding the difference  $\varphi_1^s - \varphi_1$ , were obtained by assuming that  $-\log K_i = \Delta R_{M1,2}$ . The values of  $K_i$  and  $\Delta R_{M1,2}$  are given on the graphs as functions of the pore diameters of the adsorbents,  $d$ , i.e. as  $K_i = f(d)$  and  $\Delta R_{M1,2} = f(d)$ . The quantity  $A_2 = f(d)$  is also given.

## RESULTS AND DISCUSSION

The solvent mixture, carbon tetrachloride-chloroform, used in this study as the mobile phase, can be included in systems in which interactions of the hydrogen-bond type are absent<sup>26</sup>. Soczewiński and Szumiło<sup>8,27</sup> suggested that such systems are the most suitable for theoretical considerations because of the small extent of molecular interaction between their components. These systems have no ability for association. In some cases the effect of the composition of the solvent mixture on the "chromatographic adsorption coefficient" is proportional to the solvation equilibria present in the mobile phase<sup>27</sup> and the actual situation is different from that in an ideal model system.

In a series of earlier papers<sup>11-15</sup>, the possibility of interpretation and prediction of optimum conditions for the chromatographic process was examined on adsorbents of different specific surface area and using eqn. 1. In some cases satisfactory results were obtained, but in others deviations occurred between theoretical and experimental  $R_{M1,2}$  values. The deviations were difficult to explain. They may be caused by a molecular-sieve effect or by failure to account correctly for the microporous structure of the adsorbent. In the present study, silica gel adsorbents with a different porosity, ranging from 60 to 1000 Å in diameter, were used. Other studies have been made of the properties of adsorbents in relation to porosity<sup>2,3</sup> and the number of hydroxyl groups present.

Fig. 1 shows the theoretical and experimental values of  $R_{M1,2}$  for TLAC of 1- and 2-naphthols. A fairly good agreement between these values was obtained for all four adsorbents (L, M, N, and O). The values of  $R_{M1}$ ,  $R_{M2}$  and  $R_{M1,2}$  for the naphthols change with the porosity of the adsorbent. A similar agreement between the theoretical and experimental values was obtained for 8-aminoquinoline and 8-hydroxyquinoline (Fig. 2). It is interesting that the extent of separation of the examined sub-

TABLE I

EXPERIMENTAL R<sub>F</sub> VALUES OBTAINED BY TLAC ON SILICA GEL ADSORBENTS OF DIFFERENT POROSITY (*d*)

Mobile phase, carbon tetrachloride–chloroform.

Compound	Vol. fraction of chloroform	Adsorbent			
		L ( <i>d</i> = 60 Å)	M ( <i>d</i> = 200 Å)	N ( <i>d</i> = 500 Å)	O ( <i>d</i> = 1000 Å)
1-Naphthol	0	0.03	0.09	0.12	0.22
	0.1	0.07	0.21	0.23	0.40
	0.3	0.12	0.36	0.40	0.61
	0.5	0.18	0.45	0.52	0.71
	0.7	0.26	0.50	0.58	0.75
	0.9	0.33	0.53	0.61	0.71
	1.0	0.32	0.50	0.60	0.66
2-Naphthol	0	0.02	0.05	0.08	0.14
	0.1	0.04	0.14	0.18	0.31
	0.3	0.08	0.25	0.32	0.52
	0.5	0.14	0.35	0.44	0.65
	0.7	0.20	0.43	0.51	0.69
	0.9	0.27	0.49	0.54	0.65
	1.0	0.26	0.46	0.54	0.57
Quinoline	0	0.02	0.05	0.10	0.10
	0.1	0.04	0.17	0.18	0.20
	0.3	0.11	0.29	0.27	0.37
	0.5	0.17	0.38	0.37	0.50
	0.7	0.21	0.46	0.46	0.56
	0.9	0.27	0.54	0.51	0.56
	1.0	0.24	0.44	0.52	0.54
8-Hydroxyquinoline	0	0.04	0.09	0.15	0.24
	0.1	0.15	0.31	0.35	0.56
	0.3	0.20	0.41	0.56	0.72
	0.5	0.31	0.48	0.64	0.77
	0.7	0.35	0.54	0.66	0.80
	0.9	0.41	0.55	0.64	0.77
	1.0	0.39	0.51	0.58	0.69
8-Methylquinoline	0	0.03	0.08	0.10	0.18
	0.1	0.12	0.31	0.27	0.44
	0.3	0.18	0.42	0.47	0.66
	0.5	0.28	0.50	0.68	0.75
	0.7	0.35	0.57	0.62	0.78
	0.9	0.40	0.59	0.61	0.74
	1.0	0.39	0.56	0.56	0.66
Carbazole	0	0.11	0.22	0.29	0.39
	0.1	0.27	0.45	0.47	0.62
	0.3	0.38	0.57	0.61	0.77
	0.5	0.52	0.64	0.68	0.81
	0.7	0.58	0.68	0.69	0.82
	0.9	0.62	0.70	0.68	0.78
	1.0	0.61	0.69	0.63	0.69
Fluorenone	0	0.12	0.26	0.33	0.42
	0.1	0.30	0.53	0.50	0.62
	0.3	0.41	0.62	0.65	0.77
	0.5	0.54	0.68	0.71	0.82
	0.7	0.61	0.70	0.74	0.84
	0.9	0.64	0.73	0.77	0.82
	1.0	0.63	0.73	0.74	0.79

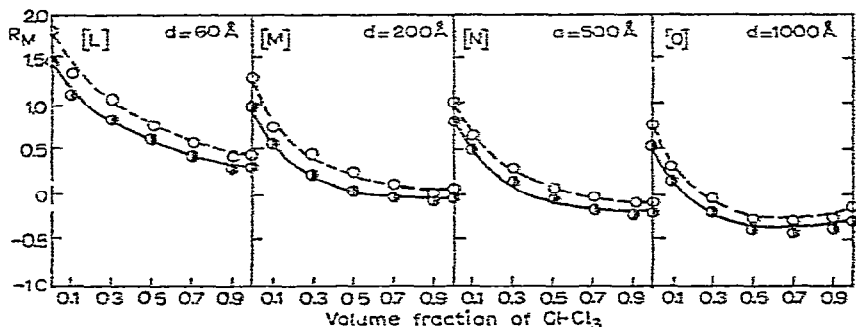


Fig. 1. Theoretical (solid and broken lines) and experimental values of  $R_{M_{1,2}}$  obtained by TLAC for 1-naphthol (●) and 2-naphthol (○) Silica gel adsorbent (pore diameter,  $d$  in Å): L (60); M (200); N (500) and O (1000). Mobile phase, carbon tetrachloride-chloroform.

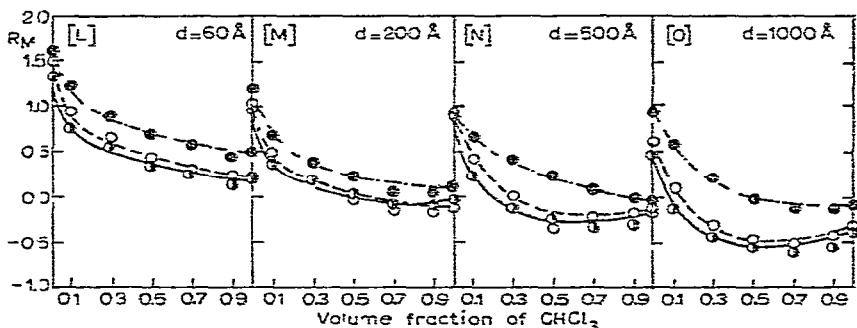


Fig. 2. Theoretical (solid and broken lines) and experimental values of  $R_{M_{1,2}}$  obtained by TLAC for quinoline (⊙), 8-hydroxyquinoline (⊕) and 8-methylquinoline (○). For details, see Fig. 1.

stances changes with the variation in porosity of the adsorbent. The different shape of the functions of 8-hydroxyquinoline and 8-methylquinoline can be explained in terms of the presence of steric effects. Good agreement between the theoretical and experimental values of  $R_{M_{1,2}}$  was also obtained for fluorenone and carbazole (Fig. 3). The tendency to formation of a minimum in the graph for the adsorbent with widest pores is interesting.

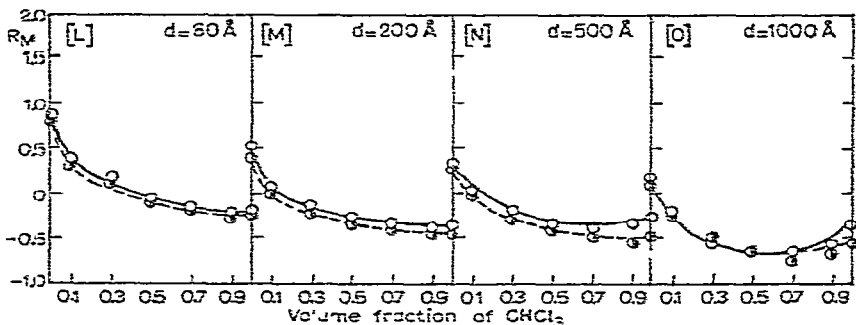


Fig. 3. Theoretical (solid and broken lines) and experimental values of  $R_{M_{1,2}}$  obtained by TLAC for fluorenone (⊕) and carbazole (○). For details, see Fig. 1.

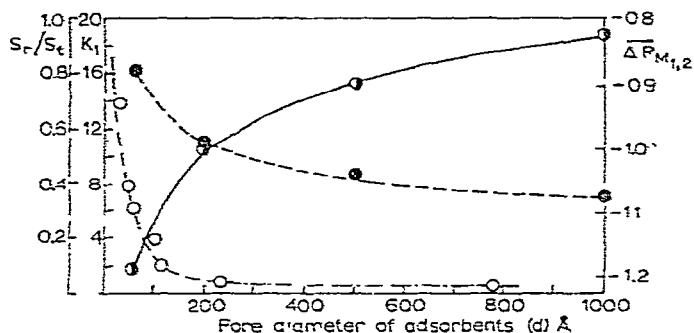


Fig. 4. Graphs of  $K_1$  (●),  $\Delta R_{M1,2}$  (○) and  $S_r/S_{r_0}$  (○) as a function of the pore diameter ( $d$ ) of the silica gel adsorbents used.

A comparison of the values of  $K_1$  with the porosity of the adsorbent provides information about the adsorption process in the present systems. It can be seen from Fig. 4 that for pore diameters of 60–200 Å (adsorbents L and M) a large change in  $K_1$  occurs. For pore diameters greater than 200 Å (adsorbents N and O), the function  $K_1 = f(d)$  is approximately linear and only changes slightly. According to Snyder and Ward<sup>3</sup>, the initial large change in  $K_1$  is due to a correspondingly large change in the number of reactive hydroxyl groups as compared with the total number of hydroxyl groups on the surface of the silica gel ( $S_r/S_{r_0}$ ). The functions  $K_1 = f(\log d)$  and  $\Delta R_{M1,2} = f(\log d)$  are presented in Fig. 5.

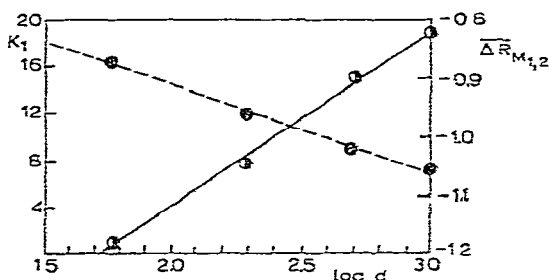


Fig. 5. Graphs of  $K_1$  (●) and  $\Delta R_{M1,2}$  (○) as a function of the logarithm of the pore diameter ( $d$ ) of the silica gel adsorbents used.

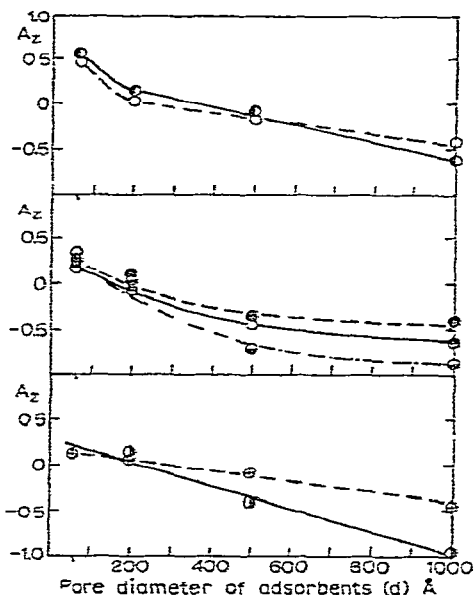


Fig. 6. Graphs of  $A_z$  as a function of the pore diameter ( $d$ ) of the silica gel adsorbents used for 1-naphthol (○), 2-naphthol (◐), quinoline (●), 8-hydroxyquinoline (◑), 8-methylquinoline (◒), fluorenone (⊗) and carbazole (⊕).

The values of  $A_z = \log k_{1,2}^{\infty}$  provide an indication of the interactions between molecules of the chromatographed substances and the solvent. Graphs of this function against the pore diameter of the adsorbent are given in Fig. 6. It can be seen that for pore diameters greater than 200 Å the values of  $A_z$  are negative. Thus the porosity of the adsorbent causes deviations from the ideal behaviour accepted in deriving eqn. 1.

In conclusion, the greatest changes in the parameters of eqn. 1 take place when the pore diameter of adsorbent is less than 200 Å. The agreement between the theoretical and experimental values of  $R_{V1,2}$  obtained on silica gel adsorbents with pore diameter 60–1000 Å is fairly good and permits an extension of eqn. 1.

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