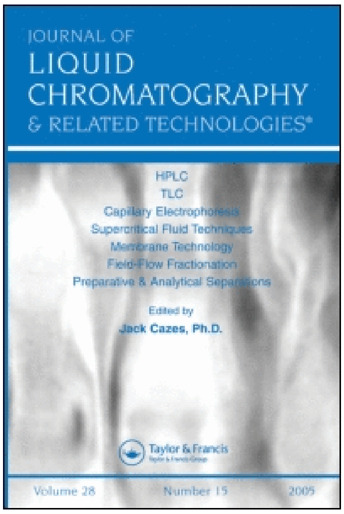

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ESTIMATION OF ADSORPTION LAYER CAPACITY BY SANDWICH THIN-LAYER CHROMATOGRAPHY

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ABSTRACT

The use of sandwich tanks with a capillary solvent delivery system permits the determination of the volume of the developing solvent in the adsorbent layer as well as the position of the solvent demixing front. Therefore, the adsorption isotherms of polar solvents from solutions in nonpolar diluents and the adsorption layer capacities can be determined in a simple manner, analogous to the column technique: Instead of determination of breakthrough volume, the solvent demixing front on the thin layer is localized by means of a series of test dyes whose spots flatten and merge on the steep solvent composition gradient. The method is illustrated for nine aliphatic ketones adsorbed from heptane and benzene solutions. The experimental results indicate different modes of adsorption from solutions in the two diluents; the surface areas corresponding to one solute molecule are also different for symmetrical dialkyl ketones and isomeric methyl-alkyl ketones.

INTRODUCTION

In spite of its great popularity, thin-layer chromatography is only rarely used as technique of physicochemical investigations. This limitation is due to several accompanying effects especially evident in saturated tanks (formation of composition gradient along the layer, evaporation and condensation of solvent vapors ahead of the solvent front) (1-3). The difficulties in interpretation of TLC data can be eliminated by preconditioning of the plates in saturated tanks or by the use of flat tanks of the sandwich type (4,5). A special type of tank was proposed by one of the authors (6): The adsorbent is saturated with the mixed developing solvent and the sample, spotted at a suitable distance behind the solvent front, migrates under conditions of equilibrium between the mobile and stationary phase. Recently Wawrzynowicz and Soczewinski (7) reported conditions under which solvent demixing, a process analogous to frontal analysis, can be eliminated; also Snyder (Ref. 1, pg. 215) derived equations for the variation of the solvent composition along the layer and the position of solvent demixing front, depending on the activity and specific surface area of adsorbent, elution strength of the solvent and its molecular area. Solvent demixing can be eliminated by wetting the adsorbent with a suitable volume of the polar solvent.

On the other hand, the formation of a sharp and easily detectable demixing front (7) may be utilized as a basis of further investigations of solvent demixing, i.e., determination of adsorption isotherms and molecular adsorption areas. The application of the sandwich tank for these investigations is facilitated by the delivery of developing solvent from a small container with a capillary siphon. The volume of the solvent in the layer can thus be found by weighing the container before and after the chromatographic run. Alternatively, the solvent can be delivered from a small horizontal burette. The loss of solvent due to evaporation is negligible; for instance, for 5 x 20 cm plates the volume of the gas phase is about 10 cm^3 and its saturation with the solvent vapours requires less than 1% of the amount needed for development.

For a monomolecular adsorption mechanism the areas corresponding to single adsorbate molecule (the so-called molecular area ω) can be calculated. This parameter is important in the description of adsorption processes. Several authors have reported values calculated by indirect methods (e.g., Ref. 8); the simplest consists in calculation from the molar volumes of pure liquid assuming spherical shape of the molecules (12). The projection areas can also be calculated from bond lengths and Van der Waals radii of the atoms; however, Snyder reported that these calculations give too low results because Van der Waals radii are derived for the crystal state where the packing of molecules is more dense than for adsorption. For instance, arbitrary addition of 0.5 Å to Van der Waals radii results in much better agreement with experimental values obtained with the BET method. McClellan and Harnsberg (8) reported the following empirical equation for the molecular adsorption area ($\omega_{ads.}$) from the projection area ($\omega_{liq.}$) calculated from the specific gravity:

$$\omega_{ads.} = \frac{\omega_{liq.} - 6.16}{0.596} \qquad (1)$$

In the present paper we will report a simple method of estimation of the adsorption layer capacity using a TLC technique which was found to give good correlations with column parameters (9).

THEORETICAL CONSIDERATIONS

The adsorbent layer is developed with a binary solvent N + B where B is a polar solvent and N - a nonpolar diluent. During development solvent B is *selectively adsorbed so that the frontal zone of mobile phase is gradually depleted of component B until a zone of pure diluent N is formed. At the same time the adsorbent layer near the start line is saturated with solvent B so that the mobile phase is in equilibrium with the adsorbent. The formation of the composition gradient along the layer is called solvent demixing and is equivalent to the frontal analysis of the developing solvent. The process is illustrated schematically in Fig. 1 in which two zones are represented. In the first (α-zone) the mobile phase contains only pure diluent N, in the second (β-zone) the composition of the mobile phase corresponds to the initial composition. If solvent B is strongly adsorbed, then the solvent demixing gradient is steep and its position can be defined as* R_{Fd}*, the ratio of distances of β- and α- fronts from the origin of the system (7). Assuming a uniform layer thickness, (constant cross-sectional areas of the phases) the fraction of volume of the mobile phase in the α-zone is equal to* $V_m(1-R_{Fd})$ *and the β-zone* $V_m \cdot R_{Fd}$*. The amount of the polar solvent B originally present in α-zone (which can be calculated from the initial concentration) is now adsorbed in the β-zone. In our considerations the adsorption of the diluent is neglected, i.e., it is assumed that the diluent molecules are completely displaced from the adsorbent surface.*

The second simplification concerns the number of moles of the adsorbate layer. Strictly, the total amount of the "i" component in the adsorption phase is given by the equation:

$$n_i^s = n_i^{\sigma(V)} + v_a c_i \qquad (2)$$

However, for not too high concentrations of the adsorbate, the second r.h.s. term can be neglected.

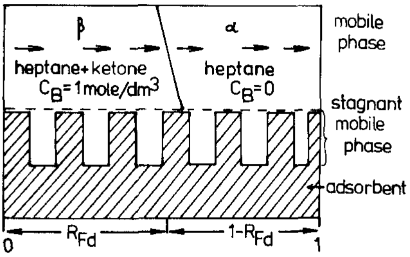

Figure 1. Schematic representation of solvent demixing in thin layer of adsorbent.

The determination of the amount of adsorbate in the β-zone permits us to calculate the adsorption layer capacity (and for monomolecular adsorption, also the molecular surface area ω^o*) from the weight of adsorbent in the β-zone and its specific surface area (*a_s*,* m^2/g*).*

For a plate that is uniformly covered with $m_{ads.}$ *grams of adsorbent, the surface area, A, of adsorbent in the β-zone (in* nm^2*) is:*

$$A = m_{ads.} \cdot R_{Fd} \cdot a_s \cdot 10^{18} \tag{3}$$

while the number of molecules of adsorbate B adsorbed on this area is equal to:

$$n = C_B \cdot 10^{-3} \cdot V_m \, (1-R_{Fd}) \cdot N \tag{4}$$

Therefore, the apparent molecular surface area:

$$\omega_{i(B)} = \frac{A}{n} = \frac{m_{ads.} \cdot R_{Fd} \cdot a_s}{C_B \cdot V_m \cdot (1-R_{Fd})} \cdot 1.66.10^{-3} \tag{5}$$

To calculate the ω_B *value it is thus sufficient to determine:*

1. *The weight of adsorbent layer on the development distance,* $m_{ads.}$ *(or in the β-zone, i.e.,* $m_{ads.} \cdot R_{Fd}$*).*
2. *The volume of the developing solvent in the layer* V_m *(difference of weights of the container before and after development divided by the specific gravity).*
3. *The* R_{Fd} *of the solvent demixing front.*

For multilayer adsorption, eq. 3 should be written as:

$$\omega^o = \bar{t} \, \frac{A}{n} = \bar{t} \, \omega_i \tag{6}$$

where $\bar{t}$ *denotes the (average) number of layers of the adsorbed solvent.*

The above considerations indicate that sandwich TLC can be used as a very simple and inexpensive method of determination of molecular adsorption areas and layer capacities. The investigations may provide additional information about the molecular mechanism of adsorption from solutions which recently became the object of controversy (13).

EXPERIMENTAL

Experiments were carried out using a modified Brenner-Niederwieser sandwich tank (6) in which a glass distributor delivers the solvent from a glass capillary siphon and a small container (ca 5 cm^3*) across the whole width of the layer. 5 x 20 cm plastic foils, precoated with 0.2 mm Si 60 silica, were used (E. Merck,* *Darmstadt, F.R.G.). To localize the solvent demixing front, HP-TLC test (E. Merck) was used. All solvents were dried over molecular sieve 4 A. The development was carried out in sandwich tanks adapted to plastic foils in a manner similar to that described in Refs. 6,7. The activated foil was placed in the tank and the test solution was spotted between the cover plates at a distance of 3 cm from the edge of the layer. A margin 1.5 cm wide was cleared of adsorbent; the development distance was 14 cm. The components of the test mixture were strongly adsorbed from the nonpolar diluent but displaced by the polar solvent so that the spots of most dyes were flattened on the solvent demixing front whose* R_F *value was then calculated from its distance from the edge of the layer and the distance of development. Then the adsorbent was scraped off from the β-zone, dried and weighed and the total volume of the solvent in the layer was determined by weighing the container. To estimate the precision of the method, ten determinations were carried out for a 1M solution of methyl ethyl ketone in heptane. The standard deviation was found to be* $\sigma_w = 0.0157$; *the surface area (for* $3\sigma_w$ *limits) was* $\omega_i = 0.2741 \pm 0.0471\ nm^2$ *which corresponds to a relative error of 6%. The experimental results (averages from 3 runs) are presented in Tables 1,2.*

RESULTS AND DISCUSSION

The nine ketones investigated belonged to two series; symmetrical dialkyl ketones (R-CO-R) and methylalkyl ketones (Me-CO-R). To secure comparable conditions, 1M solutions of the ketones were used as developing solvent. As diluents n-heptane and benzene were chosen which seemed interesting owing to recent investigations by Oscik and Goworek (10) who reported monolayer adsorption of ketones from benzene and bilayer adsorption from heptane solutions. The experimental results and adsorption areas corresponding to single molecules calculated from eq. (5) are given in Table 1 (heptane solutions) and Table 2 (benzene solutions).

The increase of molecular adsorption areas with the molar volume is different for the two series of ketones: It is markedly larger for the symmetrical ketones. For heptane solutions the log ω_i *vs. log* V^o *relationships (Fig. 2) is linear (with the exception of acetone). For methyl-alkyl ketones the relationship is less regular. Similar plots were obtained for benzene solutions, the log* ω_i *values being in most cases higher by about 0.3 units. Some irregularities in the plots are presumably due to differences in the mode of adsorption; also, the average distance between the plots obtained for heptane and benzene solution suggests predominant monomolecular adsorption for benzene solutions and bimolecular for heptane solutions (except for acetone, whose exceptionally low value of* ω_i *indicates multilayer adsorption).*

TABLE 1.

Apparent molecular adsorption areas of ketones adsorbed from n-heptane solutions (C_B = 1 mol/dm^3)

Ketone	R_{Fd}	m_{ads}(g)	V_r(cm^3)	ω_i(nm^2)
a) Symmetrical ketones				
Acetone	0.21	0.131	1.16	0.12
Diethyl ketone	0.50	0.331	1.27	0.43
Dipropyl ketone	0.59	0.426	1.12	0.77
Dibutyl ketone	0.66	0.541	1.13	1.17
b) Asymmetrical ketones				
Methyl-ethyl ketone	0.43	0.276	1.18	0.27
Methyl-propyl ketone	0.46	0.303	1.25	0.37
Methyl-butyl ketone	0.52	0.311	1.24	0.43
Methyl-pentyl ketone	0.56	0.378	1.22	0.58
Methyl-hexyl ketone	0.62	0.531	1.22	0.95

TABLE 2.

Apparent molecular adsorption areas of ketones adsorbed from 1M solutions in benzene and average number of layers for adsorption from heptane solutions ($\bar{t}_{hept} = \omega_{i(benz}/\omega_{i(hept)}$.

Ketone	R_F	m_{ads}(g)	V_r(cm^3)	ω_i(nm^2)	$\bar{t}_{hept.}$
a) Symmetrical ketones					
Acetone	0.53	0.345	1.40	0.43	3.58
Diethyl ketone	0.65	0.419	1.12	0.89	2.07
Dipropyl ketone	0.76	0.493	1.09	1.57	2.04
Dibutyl ketone	0.80	0.658	1.06	2.57	2.20
b) Asymmetrical ketones					
Methyl-ethyl ketone	0.62	0.426	1.32	0.70	2.59
Methyl-propyl ketone	0.63	0.420	1.22	0.77	2.08
Methyl-butyl ketone	0.65	0.408	1.09	0.89	2.07
Methyl-pentyl ketone	0.72	0.425	1.25	1.00	1.72
Methyl-hexyl ketone	0.72	0.557	1.14	1.45	1.53

The differentiated low ω_i vs. log V^o plots of methyl-alkyl ketones and dialkyl ketones (Fig. 2) provide some explanation of the individual properties of the two series of solvents used for the chromatography of bifunctional quinoline bases (11).

The true molecular adsorption area ω^o can be calculated from the adsorption data only for monomolecular adsorption layer of the adsorbate; in this

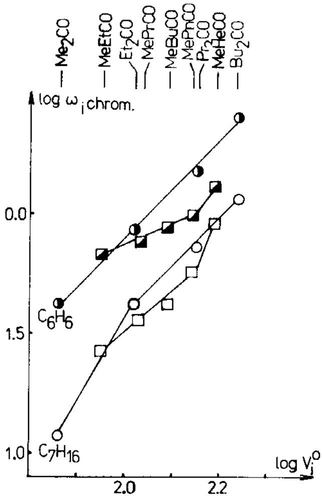

Figure 2. Log $\omega_{i\ chrom.}$ vs. log V_i^o plots of symmetrical ketones (O) and asymmetrical ketones (□) for adsorption from solutions in heptane and benzene.

case, $\omega^o = \omega_i = A/n$ (Eq. 7). For bi- and multilayer adsorption the (average) number of the layers ($\bar{t}$) should be taken into account (Eq. 6). Assuming that for benzene solutions the true ω^o values were obtained (10), the $\bar{t}$ values calculated as the ratio $\omega_{i(benzene)}/\omega_{i(heptane)}$ are given in the last column of Table 2. The values of $\bar{t}$ indicate that acetone is adsorbed from the heptane solutions in multilayer and the higher symmetrical ketones in double layers. Also methyl-ethyl ketone forms multiple layers ($\bar{t}$ = 2.5) while higher methyl-alkyl ketones form double layers with increasing tendency to lower coverages for higher homologs.

The molecular adsorption areas determined by the frontal method are higher than those calculated from other data. One of the reasons is that the adsorbent surface is assumed to be covered only by a dense layer of adsorbate molecules and any contribution of the diluent molecules is neglected which especially in the case of benzene may introduce some systematic error. Furthermore, the surface corresponding to a single silanol group is about 0.2 nm^2 so that for larger adsorbate molecules only part of the OH groups forms H-bonds with carbonyl groups. The steric factors cause that the discrepancies between the experimentally determined ω_i values and those calculated from McClellan's equation increase with the molecular size of the adsorbate (Fig. 3).

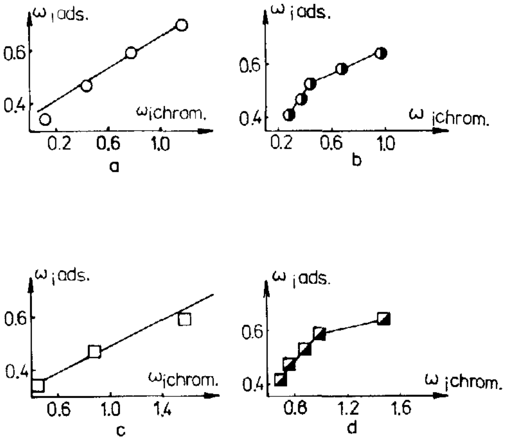

Figure 3. *Correlation between molecular areas $\omega_{i\ ads.}$ calculated from McClellan's equation and determined experimentally.*

a - symmetrical ketones + heptane
b - asymmetrical ketones + heptane
c - symmetrical ketones + benzene
d - asymmetrical ketones + benzene

The preliminary investigations reported here indicate that the modification of the sandwich TLC technique (analogous to column frontal analysis) may provide information about adsorption phenomena and especially about the molecular adsorption areas. The agreement of these conclusions with those of exact static experiments (10) is promising and indicates that it can be used at least for preliminary experiments. Its advantages are the extreme simplicity and minimal expenditure of adsorbent and solvents. For each new method or its modification, further experiments are required to secure conditions of greater accuracy and reliability of results and to define its limitations.

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