Wetting transition in alkane liquids on silanised diatomaceous gas chromatographic supports

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Abstract

For systems of an alkane stationary phase on widely used silanised diatomaceous supports, plots of retention volume of a polar solute against liquid loading show a pronounced peak. The phenomenon has been explored by systematically varying the support, stationary phase and solute. The critical loading at the steep left-hand side of the peak is independent of the polar solute used but depends on the stationary phase and support. The slope of the right-hand side of the peak is characteristic of the support, viz. Chromosorb P and Chromosorb G. Chromosorb W exhibits no peak. A previous proposal that a form of wetting transition in the liquid distribution on the support is involved has been confirmed. The results are interpreted in terms of a new version of the wetting transition model which takes into account the pore structure of the diatomaceous support as well as the surface tensions of the stationary liquid and support. The wetting transition appears to occur as liquid first spreads into pores of a size which provides the bulk of the porosity of each support. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Gas-liquid chromatography (GLC) is well established as a fast technique for studying the thermodynamics of solutions, especially at infinite dilution. The solvent most widely used in these comparative studies is squalane and much published work is based on the belief that chromatographic retention behaviour in squalane is well understood. Doubt has been cast on this belief by the findings [1–3] that for polar solutes, at a constant concentration in the two systems, squalane+silanised Chromosorb P and *n*-octadecane+silanised Supasorb, plots of V_N, the net

retention volume per gram of support, against λ, the percentage liquid loading, show a pronounced peak. In both cases the liquid phase was a nonpolar alkane and the support was a type of silanised diatomite. Diatomite supports are often silanised to reduce the retention contribution from adsorption at the support surface which may accompany absorption in the bulk solution. The silanising treatment, however, may affect a third possible source of retention, namely adsorption at the gas–liquid interface. This type of adsorption is now recognised [4–6] as important in characterising the chromatographic properties of the stationary phase in terms, for example, of Rohrschneider–McReynolds constants or Kovats retention indices. It has also recently been studied in

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other systems, such as hydrocarbons in poly(per-fluoroalkyl ether) on silanised Chromosorb P [7] and hydrocarbons in polyethylene glycol on unsilanised silica gel [8].

How the silanising treatment affects adsorption at the gas–liquid interface has been the subject of much debate [1–3,9–22]. According to one view [16,19], a liquid stationary phase such as squalane does not wet the silanised surface and the area of the gas–liquid interface is too small for adsorption to contribute significantly to retention. According to the other [3,9,15,20–22], adsorption at the gas–liquid interface is a major constituent of mixed retention mechanisms. Furthermore, the liquid phase may undergo a wetting transition and coalesce [9] at higher loadings, thereby changing the gas–liquid interfacial area and hence the contribution of adsorption at this interface to retention. The first support for this view came when Mathiasson and co-workers [1,2] observed a large peak in the plot of retention against liquid loading of *n*-octadecane on silanised Supasorb, a grey diatomite support. They attributed this peak to coalescence of the liquid phase. In doing so they implied that solute adsorption at the gas–liquid interface is an important contributor to retention. These findings appeared to be at odds with earlier studies of the related system, squalane+silanised firebrick or Chromosorb P [10,12], but were confirmed when we re-examined this squalane system [3]. While our method of data analysis [3] is very different from that used by Jönsson and Mathiasson [23], we both used elution peaks. Unlike the frontal analysis techniques previously adopted [14,18], elution techniques achieve very small solute concentrations which are not likely to eclipse the adsorption at the gas–liquid interface [15]. The real existence of the retention plot peak at normal, small, solute concentrations is confirmed by its independence of the different methods of data analysis used by the two groups of workers.

A different interpretation has since been offered for the peak in the retention plots. For the system acetone+squalane+silanised Chromosorb P, Parcher and Hung [24] actually observed two peaks at 9.5 and 11.5% liquid loading. They interpreted the first peak as arising from a form of solid support adsorption involving co-operative adsorption of solute at the triple interface between bare silanised surface,

discontinuous elements of liquid phase, and the gas phase, followed by coalescence of the liquid to a continuous film. A difficulty with this proposal is that the observed rise in retention is not usually progressive but sudden, usually occurring over only about a 0.2% range of liquid loading. Interpretation of the double-peaked plot is also hampered by lack of knowledge of the all-important solute concentration in the column.

In studies [1–3] where the solute concentration in the column has been determined, the peak in the retention plots has been interpreted in terms of a wetting transition. The influence of support adsorption on the shape of the plot is confined largely to the initial rapid decrease in retention as the liquid loading λ is increased from zero. This adsorption on a bare support surface decreases with increasing λ as liquid deactivates the highest energy sites on the surface and appears in the finest pores. In contrast to Parcher and Hung [24], Mathiasson and Jönsson showed that adsorption is insignificant at loadings in the region of the peak for the *n*-octadecane+silanised Supasorb system [1]. For the squalane+silanised Chromosorb P system, significant support adsorption may still underlie gas–liquid interfacial adsorption and sorption by the bulk liquid at peak loadings [9]. The question is whether the peak in the retention plot is due to gas–liquid interfacial adsorption or to co-operative effects at the triple interface. An interpretation of the peak in terms of gas–liquid interfacial adsorption has more comprehensive experimental support and, as we intend to show in this paper, provides a consistent pattern over six different experimental systems.

Published surface tension and contact angle data [25–29] indicate that squalane probably does not wet the silanised surface but allow the possibility of a wetting transition from a discontinuous to a continuous distribution of liquid over the surface as the liquid loading is increased. The retention plot peak was attributed by both Mathiasson and co-workers [1,2] and ourselves [3] to large changes in the liquid surface area arising from the wetting transition and pore-filling. Experimental support for this view was provided by the sharpness of the retention plot peaks, their independence of temperature and solute type [3] and their occurring at different loadings for the systems *n*-octadecane+Supasorb and squalane+

Chromosorb P. However the shapes of the retention versus loading plots show substantial differences between these two systems, and the wetting transition was variously ascribed to the left [3] right [1] hand sides of the peak. The values of the liquid loadings at the peak could not be predicted by either variant of the wetting transition model.

In order to shed light on the cause and mechanism of the wetting transition we have extended our investigation of the phenomenon to other systems by systematically varying the support, stationary phase and solute. A comparative study of the results defines the conditions for a peak to exist in retention plots and shows that pore structure plays an important role. A new model of the transition is developed in which coalescence is replaced by a sudden increase in liquid surface area associated with the known pore structure of diatomite supports.

2. Theory

The solute-stationary phase systems reported in this paper and in earlier studies [1–3] (see Table 1) gave highly asymmetric peaks (see Fig. 1), even at very small solute sample sizes. Since at these low concentrations the isotherm for partitioning of the solute in the bulk liquid stationary phase is linear, the asymmetry of the solute peak is attributable to non-linearity in one or both of the solute adsorption isotherms at the support surface and gas–liquid interface. If the peaks are strongly asymmetrical (Fig. 1), retention measurements may be made on

the diffuse side of the peak using the method of elution by characteristic point (ECP) [17]. From retention measurements for a particular solute at the same concentration on a series of columns of different loadings the adsorption and partition contributions to retention can be separated by a previously described procedure using the ECP method [3,30]. If K'_I and K'_S are the solute adsorption coefficients at the liquid and support surfaces having corresponding areas A_I and A_S per gram of support, and K_L is the solute absorption coefficient in the liquid phase having a volume V_L per gram of support, then the net retention volume per gram of support is given [9,31] by

$$V_N = K_L V_L + K'_I A_I + K'_S A_S, \tag{1}$$

where a prime (′) denotes finite concentration (non-linear isotherm region) as opposed to infinite dilution (linear isotherm region, no prime). The terms $K_L V_L (= V_N^P)$ and V_N^A, given by

$$V_N^A = K'_I A_I + K'_S A_S, \tag{2}$$

are, respectively, the partition and total adsorption contributions to net retention per gram of support. K_L is either obtained from the intercept of a plot of V_N/V_L against $1/V_L$ or calculated from the solute activity coefficient in solution if known or estimable. The adsorption contribution V_N^A is obtained by subtracting $K_L V_L$ from V_N. Variation of V_N^A with loading reflects the variation of the areas, A_I and A_S, if K'_I and K'_S and are constant. For K'_I and K'_S to be constant, the method requires retentions to be mea-

Table 1
Liquid loadings, λ_c, at the sharp rise on the left-hand side of the peak for six stationary phase + silanised support systems at 60°C

System	Stationary phase	Silanized support	Solutes	λ_c (%)	g liquid phase per m^2 support surface at λ_c
1[a]	*n*-Octadecane	Supasorb (40–60 mesh)	Butan-2-one, diisopropyl ether	4.7	0.089[d]
2	*n*-Octadecane	Chromosorb G (60–80 mesh)	Methyl acetate	4.3	0.100
3	Squalane	Chromosorb G (60–80 mesh)	Acetone, ethyl acetate, butan-2-one	1.5	0.035
4	*n*-Octadecane	Chromosorb P (90–100 mesh)	Methyl acetate, diisopropyl ether	9.0	0.028
5[b]	Squalane	Chromosorb P (60–80 mesh)	Acetone, ethyl acetate, butan-2-one	6.9	0.022[d]
6	Squalane	Chromosorb W (60–80 mesh)	Butan-2-one	—	—

[a]Ref. [1].
[b]Ref. [3].
[c]Calculated using nominal surface areas in Table 3.
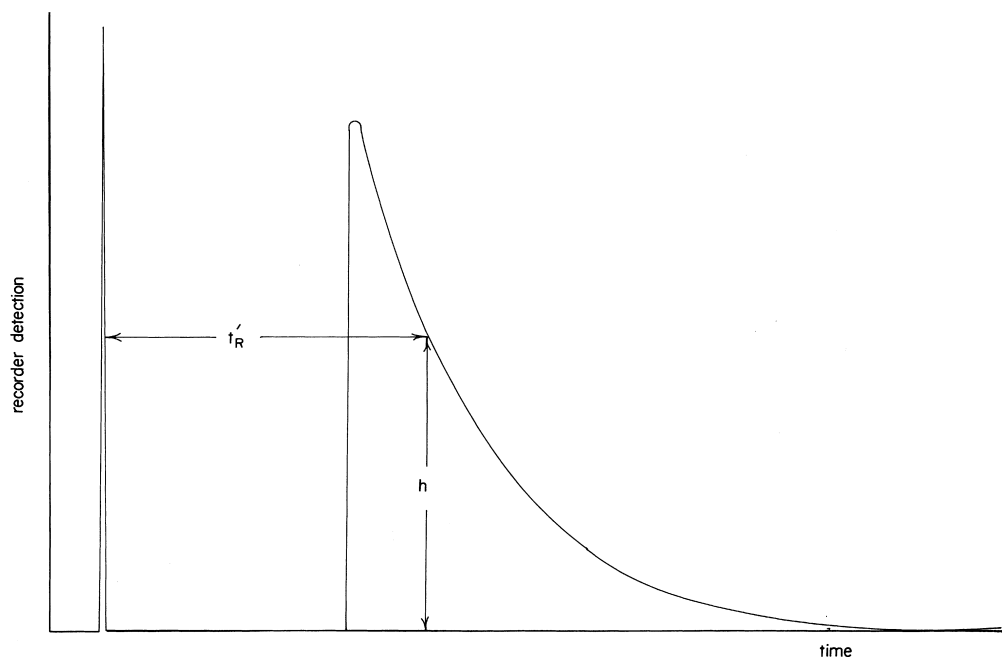[d]These values are given incorrectly in Ref. [3].

Fig. 1. ECP chromatogram obtained for diisopropyl ether at 60°C at $\lambda = 4.64\%$ n-octadecane on 90–100 mesh Chromosorb P-AW-DMCS (system 4). t'_R is the adjusted retention time from the inert gas (methane) peak to a point at height h on the diffuse side of the solute peak.

sured at a constant concentration irrespective of column loading. This is achieved by measuring the retention at the same solute concentration on each column, i.e., at the same height h on the peak in Fig. 1 [3].

3. Experimental

The experimental procedures and materials used in systems 1 and 5 in Table 1 have been described in Refs. [1,3], respectively. The equipment, procedure and materials used for system 3 were essentially the same as those for system 5, except for the use of Chromosorb G-AW-DMCS instead of Chromosorb P-AW-DMCS. The experimental procedure and materials used for systems 2, 4 and 6 are given next.

A Perkin-Elmer Auto System gas chromatograph was used, modified [32] for accurate measurement of pressure (to ± 0.5 mmHg; 1 mmHg = 133.322 Pa) at the column inlet. In all measurements the temperature inside the oven of the gas chromatograph was kept at 60°C and controlled to better than ± 0.03°C. The injector and flame ionization detector were kept at 200°C. Oxygen-free nitrogen, dried with activated

molecular sieve, was used as carrier gas. Columns were copper, of 6.35 mm O.D. Column lengths were 1 m for systems 4 and 6 and 2.5 m for system 2. The carrier gas flow-rate at the outlet of the column was measured using a soap-bubble flow meter. Flow-rates were 55 ml/min for system 4, and 30 ml/min for systems 2 and 6.

Highly pure squalane and olefin-free n-octadecane were supplied by Phase Separations, and Fluka, respectively. Methyl acetate, diisopropyl ether and butan-2-one were of the highly pure 'gas chromatography' grade supplied by BDH Chemicals. The supports for systems 2 and 6 were from Phase Separations, and the support for system 4 was from Chrompak. n-Octadecane was coated on the support from solution in n-hexane in system 4 and methylene chloride in system 2, while squalane in system 6 was coated from solution in methyl chloride. Liquid loadings and amounts of liquid in the column were obtained from at least triplicate ashings of about 1-g samples of packing, making a correction for the loss of mass on ashing the uncoated support. The ashings gave a standard deviation, expressed in terms of liquid loading, equal to or better than 0.4%. Values of V_L were calculated using the densities quoted for

n-octadecane and squalane at 60°C in Refs. [23,33], respectively. Since retention measurements on systems of the type studied are sensitive to the batch of a given support used [34], a single batch was used in all cases except system 3. Squalane columns were conditioned at 85°C for 2 h. To minimise bleeding and uncertainty in V_L, octadecane columns were not conditioned.

Injecting 10–1000 µl samples (depending on the amount of stationary phase present) of headspace solute vapour mixed with methane at 25°C gave chromatograms, such as shown in Fig. 1, which were sufficiently asymmetrical for the ECP method. The ECP requirements [35] that the self-sharpening sides of the peaks be vertical and that the maxima of peaks of different sizes should fall virtually on the common envelope of the diffuse sides were met for all the solute + stationary phase + support systems listed in Table 1 as systems 2–6. Some systems tried, such as, e.g., butan-2-one + octadecane + Chromosorb G and diisopropyl ether + squalane + Chromosorb P, did not give satisfactory ECP peaks. With systems 2 and 6 the ECP criteria were barely met, necessitating use of higher solute concentrations for system 2, as shown in Table 2.

Surface tensions of squalane and *n*-octadecane were determined by the du Noüy torsion balance method with a Fisher Scientific Surface Tensiometer model 14-812 having a platinum–iridium ring 59.45 mm in circumference. The liquids were placed in a borosilicate glass vessel thermostatted at 60±0.03°C. The results were checked by measuring the surface tension of ethylene glycol at 20°C, which gave

excellent agreement with the literature value of 47.7 mN/m.

4. Results

For squalane + silanised Chromosorb P (system 5) it has already been shown [3] that between 60 and 80°C the loading at which the stationary phase undergoes a wetting transition is independent of temperature and solute type. All the results reported in this paper are at 60°C since *n*-octadecane would bleed at higher temperatures. Running test columns with octadecane stationary phases for times much longer than those used on similar columns in this study and ashing their packings before and after use showed that, for the times of use in our experiments, bleeding of octadecane was extremely small and insignificant relative to other sources of experimental error.

Retentions at 60°C for the solutes used in systems 2–6 were measured at the loading-independent concentrations given in Table 2. An example of the resulting plots of net retention volume V_N against liquid loading λ (mass liquid ÷ [mass liquid + mass support]) is shown in Fig. 2. Except for methyl acetate in system 2 the value of $K_L V_L$ in all systems was many times smaller than V_N at the loadings of interest in the region of the peak in the plot. In these cases it was sufficient to use an estimated K_L in calculating V_N^A from V_N by subtracting $K_L V_L$. K_L values were calculated for the solutes from their activity coefficients in solution (γ), which were

Table 2
Mole fraction of solutes in liquid (x) and gas (y) phases and values of estimated activity coefficients (γ) and corresponding partition coefficients (K_L) assumed in calculating y from x and in subtracting $K_L V_L$ from V_N at 60°C

| System	Solute	x	y	γ	K_L
2	Methyl acetate	2.5×10^{-3}	5.0×10^{-3} (6.0×10^{-3})	2.5 (3.0)	32 (26.5)
3	Acetone	7.7×10^{-5}	1.46×10^{-4}	2.4	20
	Butan-2-one	7.7×10^{-5}	5.3×10^{-5}	1.8	52
	Ethyl acetate	7.7×10^{-5}	4.1×10^{-5}	1.6	67
4	Methyl acetate	5.9×10^{-5}	5.0×10^{-5}	2.5	32
	Diisopropyl ether	5.9×10^{-5}	4.1×10^{-5}	1	97
5	Acetone	1.3×10^{-5}	2.6×10^{-5}	2.4	20
	Butan-2-one	7.7×10^{-5}	5.3×10^{-5}	1.8	52
	Ethyl acetate	7.7×10^{-5}	4.1×10^{-5}	1.6	67
6	Butan-2-one	1.25×10^{-4}	1.1×10^{-4}	1.8	52
		2.50×10^{-4}	2.2×10^{-4}		
		3.75×10^{-4}	3.3×10^{-4}		
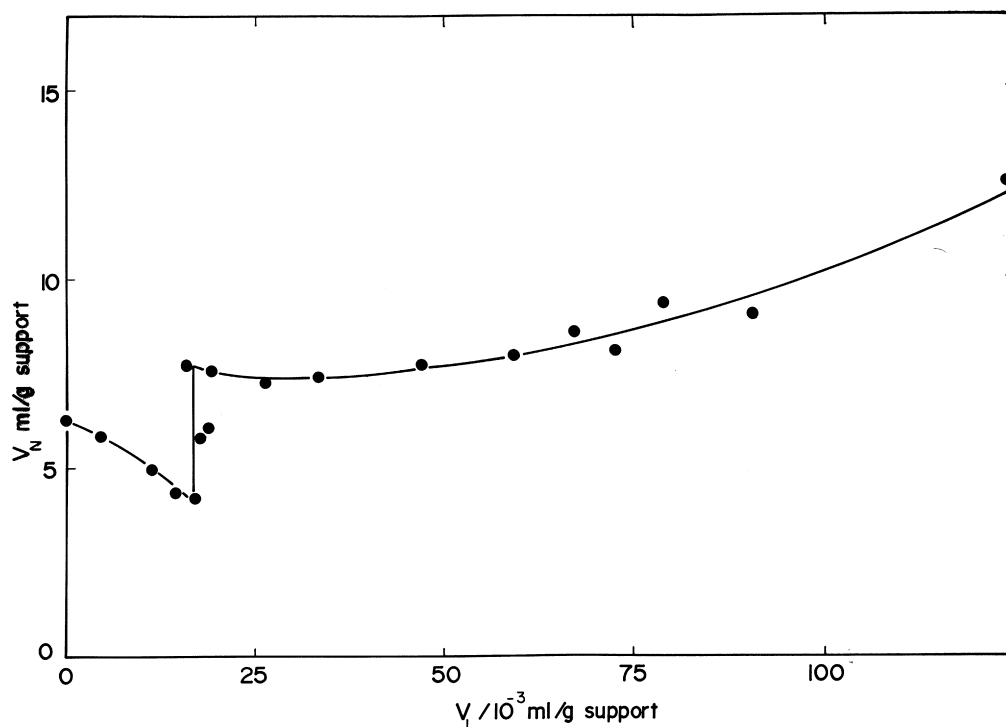
Fig. 2. Graph of net retention volume against volume of liquid phase per gram of support for ethyl acetate in squalane on 60–80 mesh silanised Chromosorb G at 60°C (system 3).

estimated from temperature-adjusted, published activity coefficients of the same or chemically similar solute–solvent systems [2,12,21,22,25,36–38] and are given in Table 2. At the low solute concentrations used in this study γ and K_L have their infinite dilution values.

For all systems the shape of the V_N–λ plots and the liquid loading at the sharp rise to the peak were independent of the solutes used. Representative plots of V_N^A against λ are given for ethyl acetate and acetone in system 3 in Fig. 3 (acetone and butan-2-one gave similar plots) and for diisopropyl ether in system 4 in Fig. 4 (methyl acetate gave a similar plot). The sharp rises to the peaks for these two systems occur at $\lambda = 1.5$ and 9.0%, respectively.

For the system methyl acetate + octadecane + Chromosorb G (system 2) the adsorption contribution to retention is very small and $K_L V_L$ is very close to V_N, due [15,20] to the high solute concentration needed for this system. As a result V_N^A values are more sensitive to the K_L value chosen which depends on the goodness of the estimate of γ from literature

data. Fig. 5 shows V_N^A against λ plots using $K_L = 26.5$ ($\gamma = 3.0$) and $K_L = 32$ ($\gamma = 2.5$). A plot of V_N / V_L vs $1/V_L$, extrapolated from low $1/V_L$ values where the adsorption terms have negligible effect on the plot, is shown in Fig. 6 to favour a K_L value of 32. A similar plot for system 4 (same solute and stationary phase as system 2) in the region of low $1/V_L$ values places K_L close to 28 but, for this system, the extrapolation error is rather high. Whichever γ is used in system 2 the position of the sharp rise in the plot at $\lambda = 4.3\%$ is unaffected.

On Chromosorb W (system 6, Fig. 7) the V_N^A–λ plots are irregular and do not exhibit a clear, distinct single peak. Plots at higher solute concentrations (Table 2) than that shown in the figure were similar but displaced vertically downwards.

For a given support (Chromosorb G in systems 2 and 3; Chromosorb P in systems 4 and 5), the wetting transition for *n*-octadecane occurs at a liquid loading 2.1–2.8 percentage points higher than the wetting transition for squalane (Table 1).

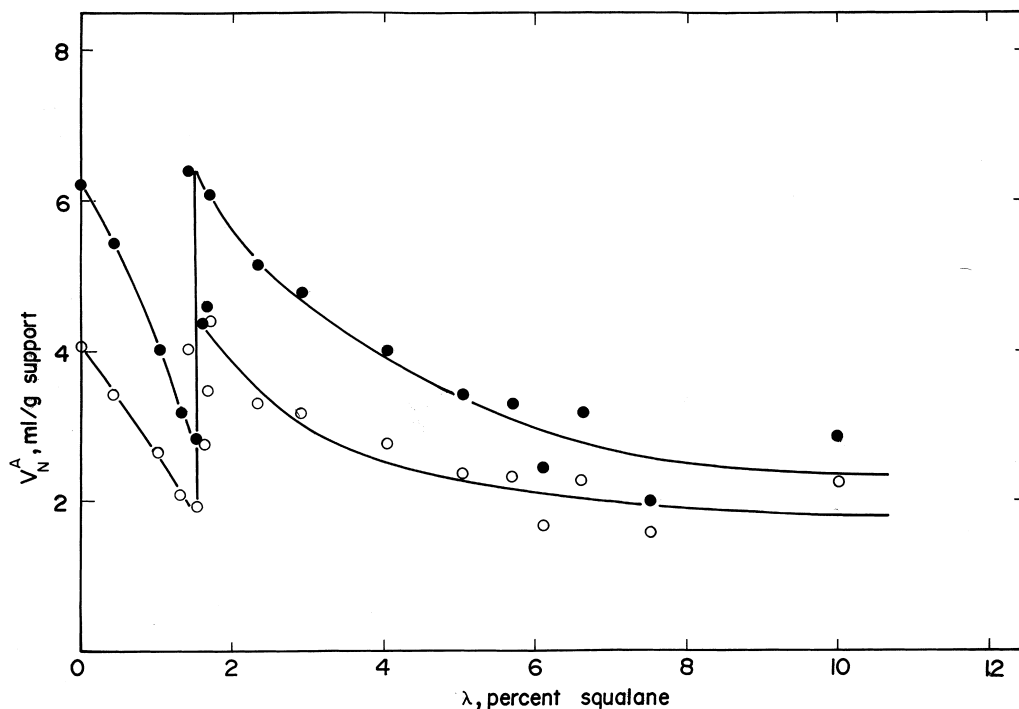We have measured the surface tensions of

Fig. 3. Graph of total adsorption contribution to retention against liquid loading for ethyl acetate (●) and acetone (○) in squalane on 60–80 mesh silanised Chromosorb G-AW-DMCS at 60°C (system 3).

squalane and n-octadecane because literature data are too few and variable for direct comparison of the two liquids. Six measurements of the surface tensions of each liquid at 60°C gave the following values: squalane, 29.24±0.04 mN/m; n-octadecane, 28.73±0.12 mN/m. These compare with literature values: squalane, 26.2–29.5 mN/m at various temperatures between 20 and 50°C [25–27]; n-octadecane, 27.5 mN/m at 30°C, 24.9 mN/m at 60°C [39].

5. Discussion

The surface tension data show that both squalane and n-octadecane only just fail to wet a silanised support surface. The critical surface tension of a trimethylsiloxy- or poly(methylsiloxane)-treated glass at 20°C is 21–24 mN/m [27–29], and the contact angle of squalane on trimethylsiloxy glass is about 46° at 60°C [27]. Diatomaceous earth supports, such as Chromosorb P and Supasorb, are composed

mainly of silica and, when silanised, may be assumed to have a similar surface tension to silanised glass. The data confirm our previous suggestion [3,9] that the surface tensions of the liquid phases are too high for the liquid to wet the support at low loadings but are sufficiently close to the critical surface tension of the support to permit a wetting transition from a discontinuous to a continuous distribution of liquid over the surface at moderate loadings. On this basis, and after examination of alternative hypotheses, it has previously been contended [1,3] that the peak in the plots of V_N^A against λ for systems 1 and 5 is due to a wetting transition, and associated change in the area of the gas–liquid interface, at a critical loading of liquid distributed discontinuously on the support.

The hypothesis of a wetting transition is substantiated by the present comparative study of the effects of variation of the stationary phase, support and solute. For all systems studied to date on pink diatomite and high density diatomite there is a sharp rise in V_N^A at a critical liquid loading which depends
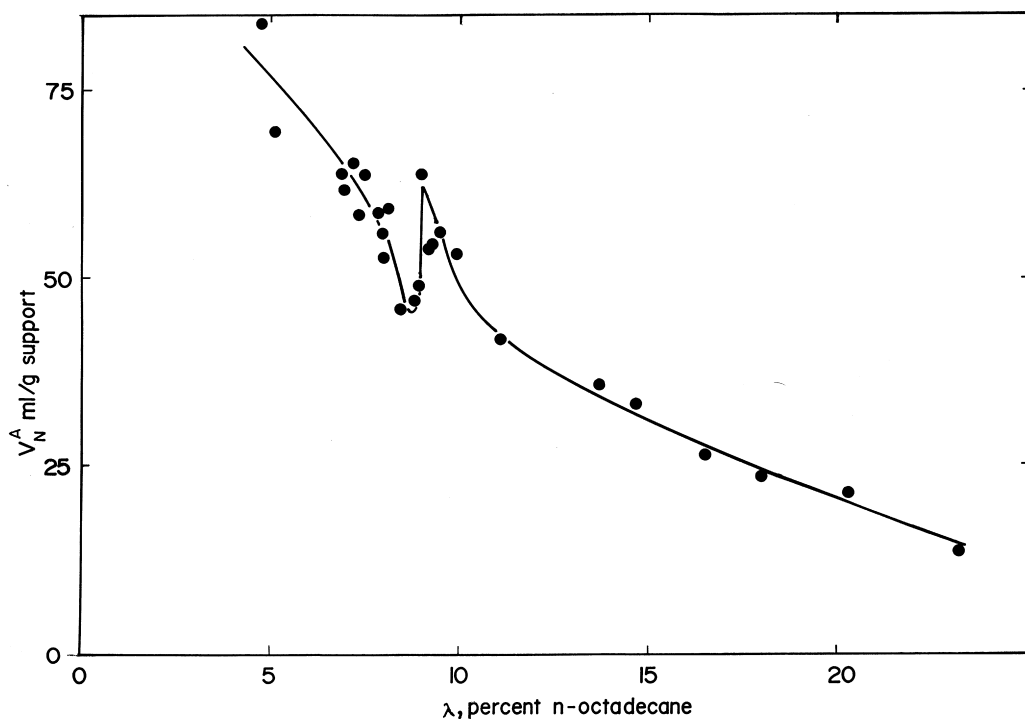
Fig. 4. Graph of total adsorption contribution to retention against liquid loading for diisopropyl ether in n-octadecane on 90–100 mesh silanised Chromosorb P-AW-DMCS at 60°C (system 4).

only on the stationary phase and support, and is independent of the solute. This critical loading is also independent of temperature, at least for the one case (system 5) studied in this way. In addition, it is independent of the method of data analysis and of the laboratory in which the measurements are conducted, as indicated by the proximity of the critical values of λ in Table 1 for systems 1 and 2 on the presumably similar high density supports, Supasorb AW-DMS and Chromosorb G-AW-DMCS. All the V_N^A–λ plots show a large loss of reproducibility in a narrow range of loading around the critical value. This feature is consistent with a wetting transition since the retention around the critical loading would be expected to be highly sensitive to the reproducibility of the support surface.

The grey high density supports (systems 1–3), which have a much lower specific surface area than pink diatomite (Chromosorb P in systems 4 and 5), show lower critical loadings than pink diatomite for both squalane and n-octadecane. The difference in critical loadings might be attributed simply to the

difference in surface areas. That this is not true is shown by the variation in the area-normalised values in the last column of Table 1. The result which correlates most consistently with the support alone is the shape of the right-hand side of the peak in the V_N^A–λ plots. On Chromosorb P, V_N^A shows a rapid initial descent from the peak for both liquids (Fig. 4 and Ref. [3]) whereas, on both the high density supports, the initial descent is always slow and progressive (Figs. 3 and 5 and Ref. [1]). On white diatomite (Chromosorb W, Fig. 7) V_N^A shows irregular variation and no clear peak is apparent in the plot. We can show that these findings help in resolving two previous models of the wetting transition and lead to the conclusion that the pore structure of the support is important in defining the wetting transition.

Two models of the wetting transition have been proposed [1,3,9]. Both attribute the peak in the V_N^A plots to coalescence of a discontinuous liquid phase. In both the liquid surface is initially limited to the meniscus in fine pores and contributes little to
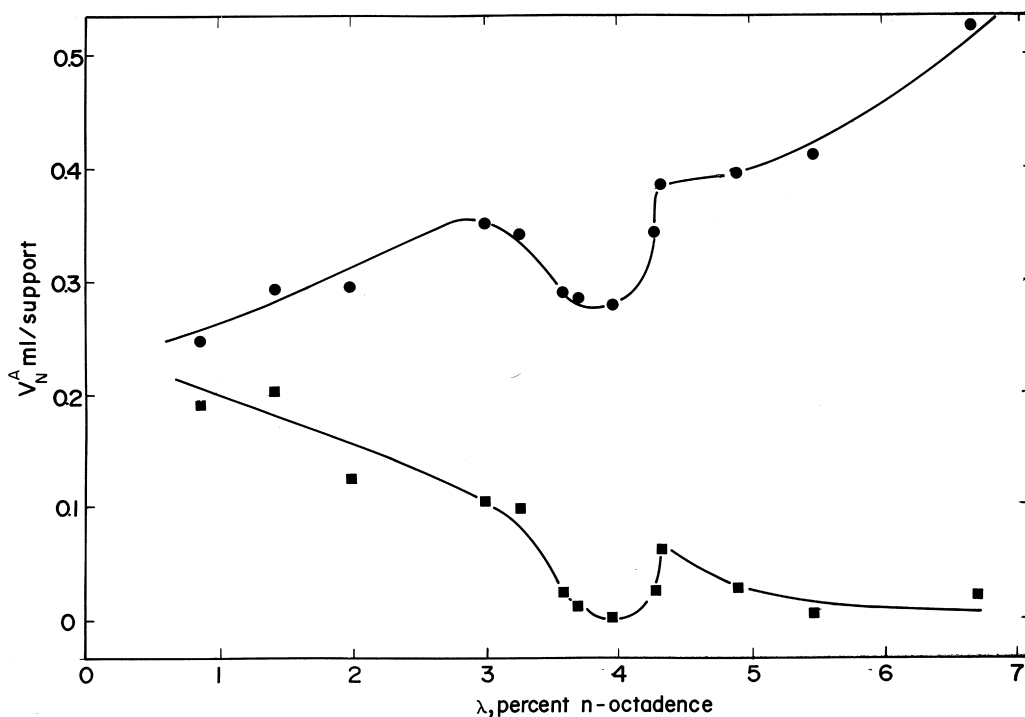
Fig. 5. Graphs of total adsorption contribution to retention against liquid loading for methyl acetate in *n*-octadecane on 60–80 mesh silanised Chromosorb G-AW-DMCS at 60°C (system 2), using $K_L = 26.5$ ($\gamma = 3.00$) (●) and $K_L = 32$ ($\gamma = 2.50$) (■).

adsorption at the gas–liquid interface. The models differ in which side of the peak they associate with coalescence. The first model [1,9,40] assumes that the discontinuous distribution consists mainly of droplets and associates the rise in V_N^A to the peak, as the loading increases, with an increase in A_I due to an increasing number of droplets. Subsequent coalescence to a film removes the large curvature of the droplets and reduces A_I and hence V_N^A. Coalescence is thus associated with the right-hand side of the peak. When the whole surface of the support is covered with a film of liquid, V_N^A continues to fall as pores are filled.

The difficulty with this model is that it depends on assuming that the units of discontinuous liquid are droplet-shaped. Mathiasson and Jönsson [1] have shown by simple geometrical argument that coalescence of contiguous spheres causes the area to decrease by a factor π, and that hemispheres give a factor of $\pi/2$. The contact angle of squalane, however, is only 46° on trimethylsiloxy glass at 60°C [27] and is likely to be similar or smaller on a

silanised diatomaceous surface. The liquid is, therefore, better envisaged as pools or patches rather than droplets. Coalescence is then more likely to result in an increase rather than a decrease in the liquid surface area. This is the basis of the second model [3] in which coalescence is associated with the left-hand side of the peak. The right-hand side is attributed solely to pore-filling.

In any model of the peak in the plot the prime need is to account for the sharp, steep rise in retention which forms the left-hand side of the peak. This is the major feature observed in all systems studied to date. The rise is so sudden and steep that it is difficult to explain merely in terms of an increasing number of droplets.

The second model associates the sharp rise at λ_c with coalescence itself. This model, too, suffers from a problem. If coalescence occurs from contiguous or nearly contiguous patches of liquid the sudden increase in area is too small to explain the large percentage rise in V_N^A observed in all systems where a peak in the plot is found. Remembering, however,
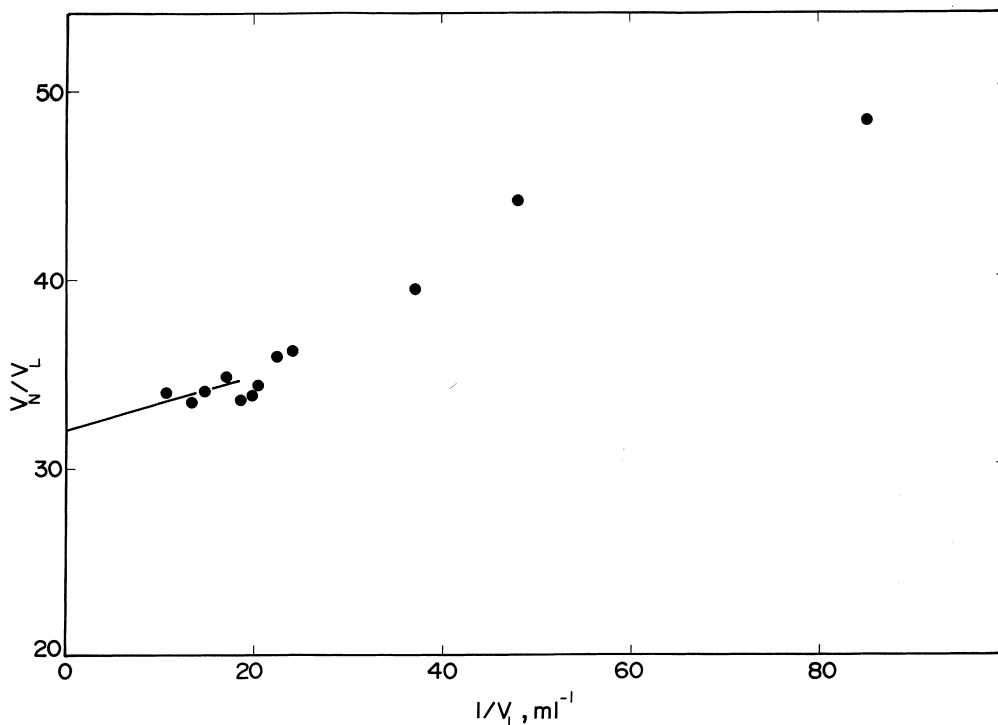
Fig. 6. Graphical estimation of the partition coefficient for methyl acetate in n-octadecane on Chromosorb G-AW-DMCS at 60°C (system 2). Only the points at high loadings (low $1/V_L$) above the wetting transition are extrapolated to $1/V_L = 0$ because A_1 changes rapidly at the wetting transition.

that the actual preparation of the packings involves evaporating solvent from a flooded packing, it is not likely that the patches of liquid at sub-critical loadings are contiguous. In the final stages of solvent evaporation, the liquid on the silanised surface probably contracts to small, non-contiguous units. To elucidate the nature of these units we need to consider the pore structures of the supports.

The three supports studied are manufactured by calcinating diatomite by different processes. Their pore sizes differ considerably. Chromosorb P has been shown by electron microscopy to possess a varied and complex structure of diatom skeletons with regular, perforated-plate or honeycomb-like structures of holes and cavities [41–43]. Although reports of the structural detail differ, they appear to agree in showing that these structures account for the bulk of the pore volume and hence of the surface area and that the holes or cavities are of diameter 0.4–2 μm. Some of the electron micrographs show

that the perforated plate structures consist of regular arrays of holes with an even more uniform size of about 0.4–0.8 μm. A small proportion of the porosity lies in smaller pores of diameter 0.1–0.4 μm. These findings agree well with porosimetric results [44–46], which show most of the porosity in 0.4–2-μm pores. In the manufacture of Chromosorb W, however, calcination with a flux destroys much of the finer diatomite structure, leaving only pores predominantly in the 2–10 μm range [41,45,46]. The pore structure of the high density supports does not appear to have been described but Saha and Giddings [45] show porosimetric plots which give a range of about 1.3–6 μm for the bulk of the porosity in Chromosorb G.

Maximum filled pore diameters have been calculated at the critical loadings, λ_c, using the data in Table 3, a squalane density of 0.783 g/ml and published porosimetry plots [44–46]. Since these plots are for a liquid which wets the whole surface,
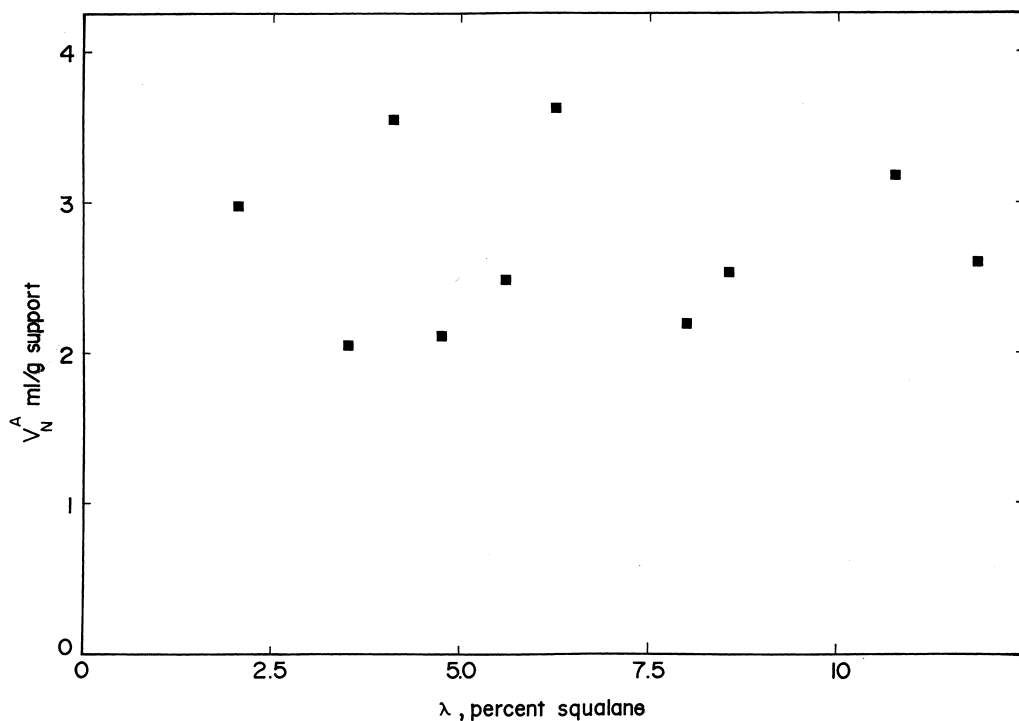
Fig. 7. Graphs of total adsorption contribution to retention against liquid loading for butan-2-one in squalane on 60–80 mesh Chromosorb W-AW-DMCS at 60°C (system 6) at $x = 1.25 \times 10^{-4}$.

filled pore diameters for our nonwetting liquids will actually be slightly larger than we have calculated, though not sufficiently so to affect the conclusions materially; the external (non-pore) surface of the support particles accounts for only about a hundredth of the total surface of Chromosorb P and about a twentieth of Chromosorb G. At the critical loading of

6.9% of squalane on Chromosorb P, calculation shows that only about 8% of the pore volume is occupied by squalane and the diameter of the largest filled pores is 0.4 μm. This pore diameter coincides with the lower limit of the diatomite structure of regular holes and cavities which appears to provide the main pore volume.

Table 3
Properties of supports

	Chromosorb P	Chromosorb G	Chromosorb W
Nominal surface area (m^2/g)[a]	3.4	0.45	1.0
Pore diameter (μm) [40,43–45]	0.4–2	1.3–6	2–10
Intra- plus extra-particle voidage [45]	0.81	0.74	0.91
Intra-particle voidage[b]	0.41	0.34	0.51
Bulk density (ml/g) [44]	0.45	0.60	0.28
Maximum filled pore diameter at λ_c (μm)[c]	0.4	1.2	—[d]

[a] A wide variety of surface areas has been reported [50]. The values quoted here are selected for likely comparability with each other and with the reported Supasorb value of 0.55 m^2/g [1].
[b] Estimated from total voidage by assuming inter-particle voidage of 0.4.
[c] Calculated from λ_c for squalane on silanised support as described in the text, assuming squalane has same density as the oil used in Ref. [45].
[d] No critical loading was found within the experimental range of λ which corresponded to filled pores of 1.2–2.7 μm diameter.

As already described, squalane has a surface tension a little too high to wet a silanised surface but still close enough to the critical surface tension for wetting the silanised surface to give a small contact angle. At $\lambda < \lambda_c$ squalane is located almost entirely in pores finer than the main 0.4–2 μm structure. For liquid in pores the unfavourable surface tension relationship for wetting is countered by the Kelvin capillary effect [47]. This attracts liquid into pores by lowering the vapour pressure at the concave liquid meniscus and so lowering the chemical potential of pore liquid. Once the finest pores are filled, with diameters less than 0.4 μm, additional liquid is attracted into the 0.4–2-μm pores which make up the characteristic diatomite structure. Because these pores comprise the main part of the porosity and vary relatively little in diameter, there suddenly becomes available to the liquid a large number of pores, the narrowest of which have a common diameter of about 0.4 μm. The total area of liquid surface suddenly expands rapidly with increasing loading as small pools of liquid appear in many pores of the main structure. The effect is enhanced because the porosimetric plot [45] is linear in pore volume terms for pore diameters over 0.4 μm and so is non-linear in pore area terms, with the surface area concentrated towards the narrowest pores of the main structure. The combined effect is a steep rise in A_I which accounts for the steep rise in V_N^A at $\lambda_c = 6.9\%$. Subsequent pore filling begins in 0.4-μm pores, causing A_I to fall, rapidly at first, then more slowly as the process spreads to larger pores within the narrow size range of the main structure.

Similar behaviour appears to occur on Chromosorb G. The maximum filled pore size for squalane at $\lambda_c = 1.5\%$ is calculated to be 1.2 μm. This is again close to the lower limit of the region (1.3–6 μm) of Saha and Giddings' [45] porosimetry plot for Chromosorb G which shows the most rapid variation of pore volume with diameter. These pores, however, are about three times larger than at λ_c on Chromosorb P, so the Kelvin capillary effect is much reduced and pore-filling proceeds more slowly, over a wider range of liquid loading. This results in the descending right-hand side of the peak in the V_N^A–λ plot being characteristically less steep than for Chromosorb P.

In Chromosorb W much of the characteristic diatomite structure is destroyed and the bulk of the remaining pores are so large (2–10 μm) that the Kelvin capillary effect is too weak to counter the unfavourable surface tension relationship for wetting on the silanised surface. The absence of a distinct peak in the V_N^A plot helps to confirm the model in which the wetting transition is associated with pore size, since pore size is the principal characteristic which distinguishes Chromosorb P and G, on the one hand, from Chromosorb W on the other. With no significant Kelvin effect operating, the liquid distribution on Chromosorb W is not well defined and becomes determined instead by the surface energy distribution, to whose reproducibility the liquid distribution will be very sensitive. This, together with the fact that Chromosorb W is notoriously more friable than the other two supports when handled, may help to explain the irregular variation in the V_N^A plot in Fig. 7.

The octadecane plots (systems 1, 2 and 4 in Table 1) give λ_c values 2.1–2.8 percentage points higher than the respective corresponding squalane plots (systems 3 and 5). This is explicable by octadecane having a surface tension a little lower than squalane but still above the critical surface tension of the silanised surface, giving a smaller contact angle and requiring less curvature in the filled pore meniscus to counter the unfavourable surface tension relationship. The amount of liquid occupying the subcritical pores when 'filled' would then be rather larger for octadecane than squalane, as confirmed experimentally. That the difference is substantial may be due to the 'short, fat' character of the characteristic diatomite pore structure seen in electron micrographs.

The model we have described appears to be consistent with the data arising from the present, comparative study of the effects of solute, support and liquid phase. In effect, it provides a third model, sharing a common basis with the earlier two, but replacing the concept of coalescence by one of spreading of liquid into a multiplicity of previously unoccupied pores of similar size, which provide the bulk of the support's surface area. It provides a more satisfactory explanation of the main features of the comparative data.

The model is supported by independent evidence from electron microscopy [48] that squalane is located in the pores of Chromosorb P-HMDS. A

droplet distribution appears to occur only when squalane is coated on a low surface energy support such as the porous organic polymer Chromosorb 101 [48], on which squalane presumably has a contact angle greater than 90°.

6. Conclusions

The existence of a wetting transition and the presence of a large contribution to retention from liquid surface adsorption on silanised GLC packings are closely associated phenomena. They occur only when the surface tension of the non-wetting liquid exceeds the critical surface tension of the support by an amount small enough to give a contact angle which, though not zero, is still low. Squalane and *n*-octadecane fulfil the condition when used on silanised supports, as they often are in order to minimise peak tailing. Liquids such as glycerol and PEG-400, however, with a much higher surface tension, have a large contact angle and appear to have only a small liquid surface area [16]; electron micrographs suggest that PEG-400 is not distributed throughout the interior and exterior of each support particle like squalane but is largely restricted to the outer surface of the particle as a thick non-uniform layer [49].

According to the new data and model presented in this paper, the existence of a sharp wetting transition depends not only on surface tension relationships but also on the pore structure of the silanised support. Of the diatomaceous earth supports, only the pink support and, to a lesser extent, the high density supports, possess the necessary combination of porosities: a small porosity in pores sufficiently fine to tie up a quantity of liquid by capillary action, and a large porosity in larger pores, characteristic of the diatomite structure, having a narrow spread of pore size but still small enough to exhibit capillary action. The resulting V_N^A–λ plot shows a large peak whose left-hand side represents the wetting transition. In contrast, the pores of the white support are too large for a wetting transition to exist.

The absence of a wetting transition on the white support thus does not mean that adsorption contributions to retention are absent. Nor, evidently, does the practice of silanising diatomaceous supports neces-

sarily simplify the adsorption behaviour. Whenever the thermodynamics of solution of a polar solute are studied in a less polar stationary phase it is necessary to anticipate and separate mixed retention mechanisms. This requires varying the liquid loading and using either Mathiasson and Jönnson's experimental procedure [1] or the procedure used in the present work.

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