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MIXED RETENTION MECHANISMS IN GAS-LIQUID CHROMATOGRAPHY

II. CONTRIBUTIONS OF ADSORPTION AND PARTITION TO THE RETENTION VOLUME IN SYSTEMS WITH POLAR SOLUTES AND NON-POLAR STATIONARY PHASE ON A SILANIZED SUPPORT

LENNART MATHIASSEN and JAN ÅKE JÖNSSON

Department of Analytical Chemistry, University of Lund, POB 740, S-220 07 Lund (Sweden)

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SUMMARY

The contributions from adsorption and partition at infinite and finite solute concentrations have been investigated for a gas-liquid chromatography system with a silanized support, non-polar stationary phase (octadecane) and polar solutes (ethyl methyl ketone and diisopropyl ether). It was found that the contribution from adsorption varied strongly with the sample size. The variation of adsorption with liquid loading at infinite solute concentration showed a rapid decrease between 0 and 1% loading followed by a rapid increase at *ca.* 5%. To explain this behaviour it is suggested that one part of the stationary phase is blocking the most active sites (dominating at very low liquid loading) and another part is forming droplets on the surface of the support. The variation of adsorption with liquid loading for loadings higher than *ca.* 2% can be explained by the variation of the gas-liquid interfacial area with liquid loading. It is therefore concluded that the dominant adsorption mechanism for loadings higher than *ca.* 2% is the adsorption at the gas-liquid interface.

INTRODUCTION

The existence of concurrent adsorption phenomena in gas-liquid chromatography (GLC) has been known for a long time. As early as in 1961 Martin¹ incorporated a term in the usual equation for the retention volume to correct for the adsorption at the gas-liquid interface. The magnitude of adsorption at the gas-liquid interface in different GLC systems has been controversial ever since. The discussion has been reviewed by Locke² in 1976. The question of the relative importance of adsorption at the liquid surface and at the support surface, especially in systems with polar solutes and non-polar stationary phases, is not yet settled. As late as December 1976 Serpinet³ argued against Conder⁴ on this question.

It is the purpose of this paper to contribute to the understanding of the role that liquid surface adsorption and support surface adsorption play in GLC systems with polar solutes, non-polar stationary phases and silanized supports.

THEORETICAL

In Part I⁵ we have developed an equation which makes it possible to obtain the contributions of adsorption and partition at different sample sizes from measurements on only one column:

$$V_N = A + \frac{C}{\left[1 + B \left(\frac{n_t}{V_N + V_M}\right)^D\right]^2} \quad (1)$$

Eqn. 1 is fitted to the experimental data. V_N is the corrected retention volume and V_M is the void volume. A is the contribution from bulk solution which in the present system is independent of the sample size⁵, and the second term is the contribution from adsorption when the injected amount is n_t moles. Thus, C is the contribution from adsorption at zero sample size. B and D are constants for a given column. For $n_t = 0$, eqn. 1 gives the retention volume at infinite dilution so that the influence of non-linearity of the isotherms is eliminated.

The validity of eqn. 1 has been demonstrated in Fig. 2 of Part I⁵ where plots of A versus the volume of the stationary phase gave straight lines for ethyl methyl ketone and diisopropyl ether. Furthermore, the partition coefficient obtained agreed well with those determined by static measurements.

EXPERIMENTAL

We have used the same equipment, procedure and experimental conditions as in Part I⁵. The same solutes, ethyl methyl ketone and diisopropyl ether, were investigated on octadecane columns with silanized support (Supasorb AW DMS, 40–60 mesh) at 333.2 °K.

RESULTS AND DISCUSSION

The experimental points for the variation of retention volume with sample size were fitted to eqn. 1 for eleven columns with different stationary phase loadings. Some of these fits have been illustrated Part I⁵. Knowing the values of the constants A , B , C and D in eqn. 1 for each system, the percentage of adsorption at different sample sizes has been obtained. Fig. 1 shows these results with ethyl methyl ketone and diisopropyl ether as solutes for a number of liquid loadings. It is interesting that there is no simple trend in the contributions from adsorption at the same sample size for different liquid loadings. This indicates that at least two adsorption mechanisms operate.

Table I gives values of the constants A and C in eqn. 1 for different columns together with liquid loading and amount of packing. The contribution from adsorption at infinite dilution is equal to C and the corresponding value of the retention volume is equal to $A + C$. The value of the constant D in eqn. 1 varied between 0.40 and 0.65. No trend in D could be observed either with respect to liquid loading or percentage of adsorption on the different columns.

The variation of the retention volume per gram of packing at infinite dilution,

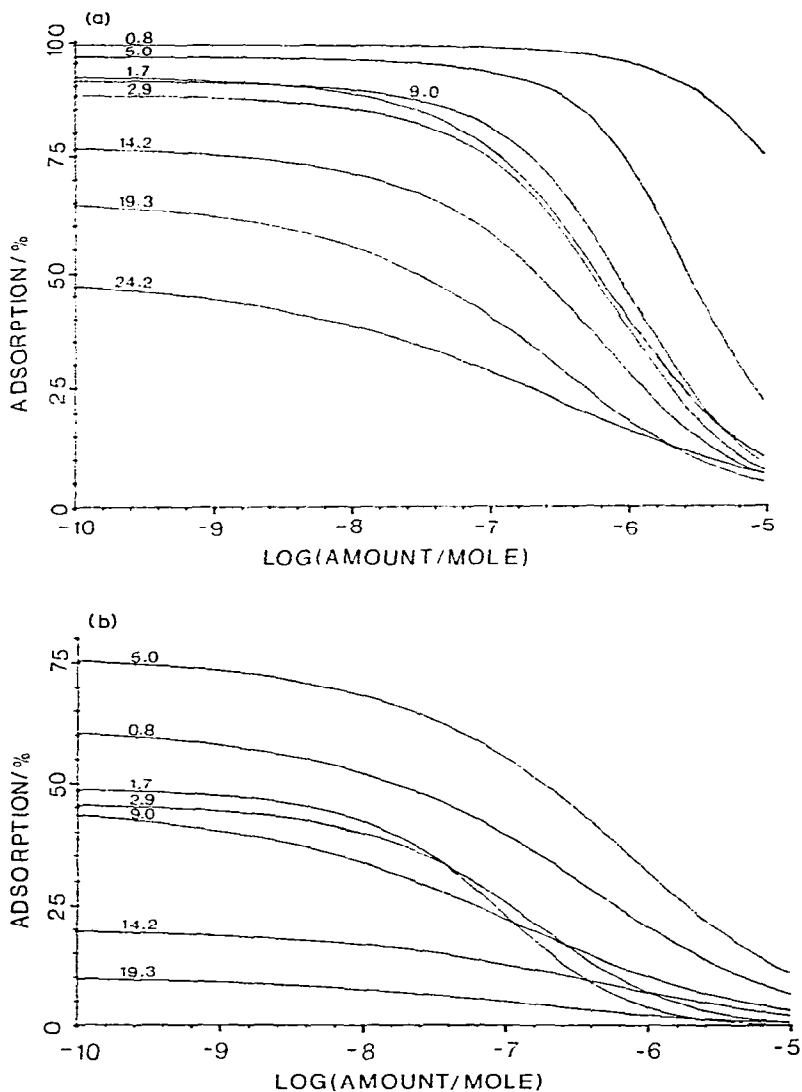


Fig. 1. Percentage of adsorption of the total retention volume for ethyl methyl ketone (a) and diisopropyl ether (b) plotted against injected amount with octadecane as stationary phase on silanized support. The percentage of liquid loading for the different packings is marked on each curve.

$V_N(0)$, against liquid loading for ethyl methyl ketone and diisopropyl ether is given in Fig. 2. $V_N(0)$ is equal to $A + C$ divided by the corresponding amount of packing from Table I. The variation of the percentage of adsorption at infinite dilution of the solute [$C \cdot 100/(A + C)$ in Table I] is shown in Fig. 3. These diagrams also indicate that at least two adsorption effects are present. If the only adsorption that occurred in the systems was that at the support surface the increase of $V_N(0)$ in Fig. 2 for liquid loadings greater than *ca.* 1% would be approximately linear and due to the increasing volume of the stationary phase. The decrease in the percentage of adsorption for ethyl methyl ketone and diisopropyl ether in Fig. 3 would be curves without any maxima.

TABLE I

VALUES OF THE CONTRIBUTIONS FROM PARTITION (*A*) AND ADSORPTION (*C*) TO THE TOTAL RETENTION VOLUME AT INFINITE DILUTION OF DIISOPROPYL ETHER AND ETHYL METHYL KETONE

A and *C* have the same meaning as in eqn. 1.

Loading (%)	Amount of packing (g)	Diisopropyl ether		Ethyl methyl ketone	
		<i>A</i>	<i>C</i>	<i>A</i>	<i>C</i>
0	3.37	0.40*	19.94	0.26*	103.17
0.8	2.98	2.60	4.22	0.14	24.43
1.7	3.16	7.23	6.92	3.68	38.37
2.9	2.93	10.21	8.62	5.47	41.51
4.0	3.12	14.35	12.43	7.06	49.83
5.0	3.04	15.04	49.55	11.60	307.16
7.4	3.05	24.42	38.65	11.31	282.98
9.0	3.36	39.82	33.53	24.04	296.63
14.2	3.46	66.20	16.54	38.95	130.84
19.3	3.75	92.64	10.53	52.95	102.14
24.2	3.93	124.50	6.95	70.16	70.67

* The deviation from zero is not statistically significant. See also plot of *A* against liquid phase volume in Fig. 2 in ref. 5.

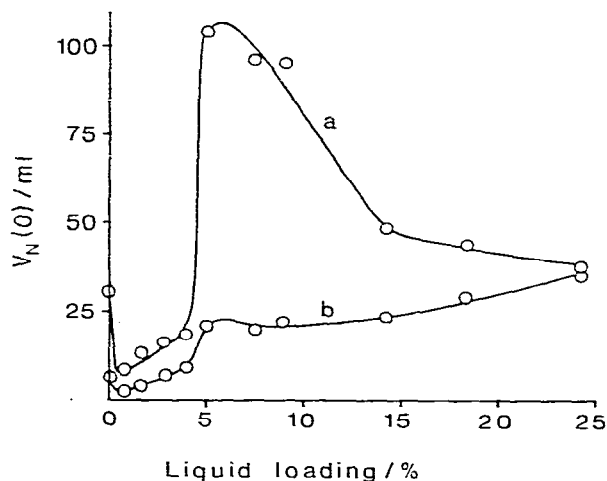


Fig. 2. Retention volume per gram of packing at infinite dilution, $V_N(0)$, for ethyl methyl ketone (a) and diisopropyl ether (b) plotted against liquid loading of octadecane on silanized support.

Fig. 4a and b shows the variation of the total adsorption per gram of support with liquid loading at infinite dilution of the solute. Although the magnitude of the effects are much greater for ethyl methyl ketone than for diisopropyl ether the shapes of the curves are very similar. This indicates that the same retention mechanisms operate in the two systems.

The most striking features in Fig. 4 are the rapid decrease of the adsorption in the region of low coverage and the rapid increase of the adsorption in the region of

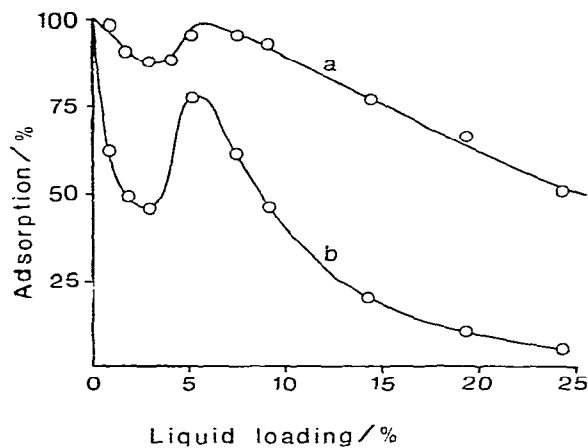


Fig. 3. Percentage of adsorption of the total retention volume, at infinite dilution, for ethyl methyl ketone (a) and diisopropyl ether (b) plotted against liquid loading of octadecane on silanized support.

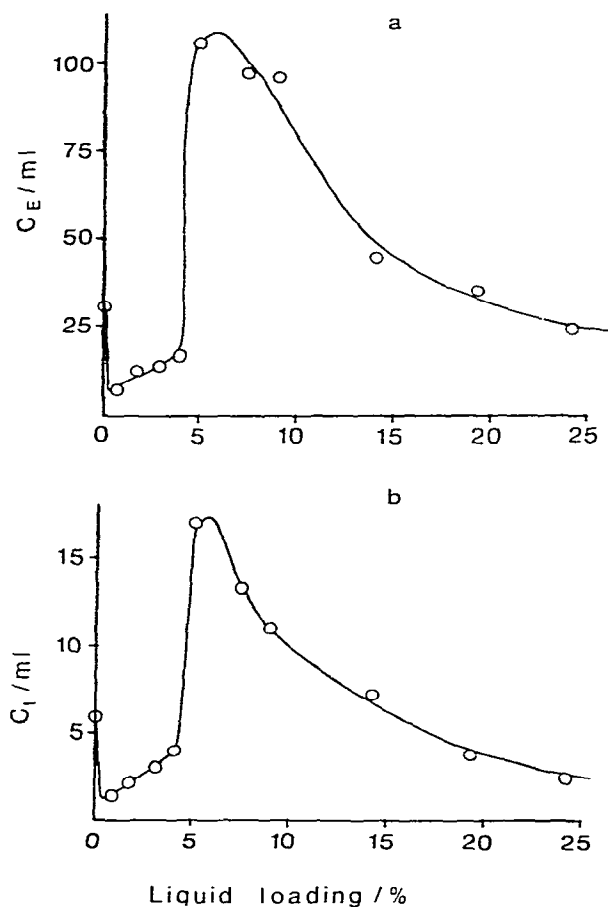


Fig. 4. Adsorption per gram of support, at infinite dilution, of ethyl methyl ketone (a), C_E , and diisopropyl ether (b), C_I , against liquid loading of octadecane on silanized support.

4–6% coverage to a maximum value which is much higher than the value for adsorption on pure support. Since the solutes are at infinite dilution this behaviour is not due to non-linear isotherms. We suggest that one part of the liquid phase is blocking the most active sites of the support and another part is forming small drops on the surface of the support. The existence of droplets on the silanized support is possible because of poor wetting of the support by non-polar stationary phases such as octadecane. The lack of wetting has been discussed by Serpinet³ who compares surface tensions of alkanes with those of polymethylsiloxane layers. Also Conder *et al.*⁶ have discussed the situation of a non-wetting stationary phase and propose that the liquid is distributed as isolated droplets which coalesce for higher loadings and give a liquid film on the support.

In the low coverage region the only process is blocking of the most active sites. The surface of the support is heterogeneous with adsorbing sites of different energies. For each loading there is a certain adsorption constant at the solid surface which rapidly decreases as the most active sites are blocked until the whole support surface is covered with stationary phase. It is expected that the most active sites are blocked in the region of very low percentage of liquid loading. As a result of the rapid decrease in the adsorption constant, the contribution from adsorption at the support surface rapidly decreases. We expect the blocking of the most adsorptive sites to take place preferably in the very small pores, which are always present to some extent in this type of totally porous support. This means that for low liquid loadings the liquid surface is principally limited to the meniscus of the capillary condensate and therefore small compared with the area of the support. Thus the adsorption at low liquid coverage is almost entirely due to support surface adsorption. An inspection of Fig. 4 shows that this contribution has almost levelled off at a loading of less than 1% for both ethyl methyl ketone and diisopropyl ether. This means that the large increase in the adsorption between 4 and 6% liquid coverage must be due to liquid surface adsorption. Since the liquid surface is essentially homogeneous, the adsorption constant at the liquid surface will be nearly independent of the liquid loading. Thus the large variation of the adsorption in the region of higher coverage depends on the variations of the liquid surface area.

When the most active sites of the support are covered with stationary phase the formation of droplets begins. With increasing liquid loading more and more droplets are formed and the area of the liquid surface increases. When so many droplets are formed that the distances between them are small, the droplets coalesce to spots of liquid film resulting in a substantial decrease of the liquid surface area. With further increase of liquid loading the area of the film will continue to decrease because of smoothing of cavities and filling of larger and larger pores (a process which starts at a liquid loading of 0%). The change of the area due to this process would be very similar to the variation of the adsorption with stationary phase loading in Fig. 4. Conder *et al.*⁶ have considered the variation of the liquid surface area with stationary phase loading for a non-wetting stationary phase (Fig. 2b in ref. 6). It seems however that they have somewhat underestimated the magnitude of this variation. The variation of the liquid surface area with stationary phase loading is discussed more in detail in the Appendix.

It is interesting to compare our model of liquid distribution on silanized support with other models. In the model of Serpinet³ the stationary phase is assumed to

be exclusively located in the capillaries. This model can explain the decrease in adsorption for low liquid loading but is not consistent with the rapid increase of adsorption at a loading of *ca.* 4–6%. Indeed, Fig. 6 in the paper of Serpinet⁷, which shows the change of retention volume with liquid loading in the low coverage region, is very similar to the results in Fig. 2. Giddings⁸ has proposed a distribution of the liquid on an unsilanized support between a capillary condensate and a thin liquid film. In this model the surface area of the liquid film increases up to the point of a monolayer which, according to Conder *et al.*⁶, is reached for a loading of *ca.* 0.1% on a support with a surface area of 2 m²/g. This means that for coverages higher than *ca.* 0.1% the area of the liquid surface, and hence the liquid surface adsorption, decreases. Since the adsorption at the support must decrease with increasing loading due to the blocking of the active sites with stationary phase, the net result must be a decrease in adsorption from the point of monolayer formation (and probably in most cases from pure support). Therefore the increase of the adsorption at 4–6% in our system cannot be explained with Giddings' model either.

The extent of adsorption at the support surface and at the gas-liquid interface has been discussed by several authors (see the review of Locke²). Our results, see Fig. 4, show that the extent is greatly dependent on the percentage of liquid loading. For a loading less than *ca.* 0.5%, adsorption at the support surface is dominant and this effect decreases rapidly. Already at 2% liquid loading the adsorption at the gas-liquid interface seems to dominate, and at a liquid loading of *ca.* 6% more than 95% of the total adsorption is due to liquid surface adsorption. The interpretation of the experimental results in terms of dominance of one adsorption isotherm for each investigated column loading also explains the fact that eqn. 1, which contains only one adsorption isotherm, describes well the variation of the retention volume with sample size for all liquid loadings.

Conflicting results have been reported for the retention behaviour of polar solutes on nonpolar stationary phases. We think that in many cases the discrepancies are due to the fact that in the early investigations the large influence on the retention volume of the sample size was not fully recognized. For example, the studies of Martin¹, Parcher and co-workers^{9,10}, Liao and Martire¹¹ and Serpinet⁷ on similar systems to ours employed a sample size range where the retention volume is expected to vary with sample size. A linear extrapolation to infinite dilution will also give different results depending on the sample size where this extrapolation starts. The extrapolation procedure introduced by Conder¹² and used elsewhere¹⁷ is the only one hitherto published that can be expected to give accurate values of the retention volumes at infinite dilution.

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APPENDIX

Variation of liquid surface area with liquid loading

Simple model. Suppose that, due to the lack of wetting of the support, the liquid phase is distributed as small droplets on the support. Consider n droplets with radius r on a grain of a porous support with a surface area A . With x = volume of liquid per unit area:

$$x = \frac{4}{3} \cdot \pi \cdot r^3 \cdot \frac{n}{A} \quad (\text{A1})$$

If the contact area between the droplets and the support is assumed to be zero the area, A_d , of the droplets in contact with the gas phase will be:

$$A_d = 4\pi \cdot n \cdot r^2 \quad (\text{A2})$$

Combining eqns. A1 and A2 gives

$$A_d = C \cdot x \quad (\text{A3})$$

with

$$C = \frac{3 \cdot A}{r} \quad (\text{A4})$$

Suppose that, when increasing x , new droplets with the same radius r will form, until the droplets are so near to each other that their cross sections touch and they coalesce to a liquid film for $x = \bar{x}$. At this loading the area of the liquid will cover the area of the underlying support (for each droplet a square with side equal to $2r$) and the area of the liquid film, A_f , will be:

$$A_f = n \cdot (2r)^2 \quad (\text{A5})$$

Combining eqns. A1, A3 and A5 gives:

$$A_f = \frac{C \cdot \bar{x}}{\pi} \quad (\text{A6})$$

A comparison of eqns. A3 and A6 shows that at $x = \bar{x}$ the area will decrease by a factor π . Fig. A-1a shows a diagram of this simple model where A_{LS} is the gas-liquid interfacial area. If instead the formation of hemispherical droplets on the support is considered, the area of the droplets will decrease by a factor of $\pi/2$.

Refined model. Suppose:

(1) The formation of droplets begins at $x = x_0$. (Some liquid volume is used to block the most active sites on the support.)

(2) The formation of a liquid film from the droplets starts at $x = h\bar{x}$ where $h < 1$.

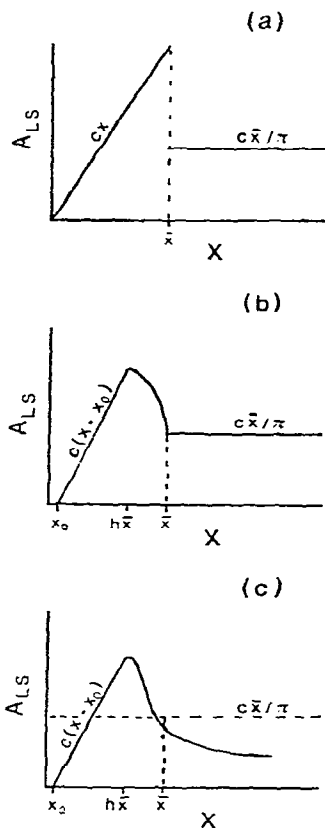


Fig. A-1. Gas-liquid interfacial area, A_{LS} , for a non-wetting stationary phase plotted against volume of liquid per unit area, x .

(3) The fraction of droplets which form a film increases linearly from 0 at $x = h\bar{x}$ to 1 at $x = \bar{x}$. The influence on the liquid surface area, A_{LS} , from the three statements above is given in Fig. A-1b.

(4) When the droplets have coalesced to a liquid film the gas-liquid interfacial area will decrease in the same way as on a wetted support due to filling of pores and smoothing of cavities. This means that according to Berezkin¹⁴ the liquid surface area is a linear function of $1/V_L$ where V_L is the volume of the stationary phase. The approximate variation of the gas-liquid interfacial area with x in this case can be seen in Fig. A-1c.

In the models above it has been assumed that the droplets are of equal size, size, which of course is an oversimplification. However, a distribution of droplets of not too widely differing size will have little effect on the general shape of the curve in Fig. A-1c. The assumption that the size of the droplets is independent of the liquid loading can also be discussed. An increase of the drop size at higher loadings would lead to a slower increase of the area of the gas-liquid interface for $x < h\bar{x}$, bending the line in Fig. A-1c for $x < h\bar{x}$ towards the x axis, but the decrease of the liquid surface area from $x = \bar{x}$ would be essentially unchanged.

Comparison of the model with experimental results. The model as illustrated in Fig. A-1c can be compared with the experimental results as shown in Fig. 4. The relation between x and the liquid loading F_x is

$$x = \frac{F_x}{100 - F_x} \cdot \frac{1}{\delta_e \cdot a_1} \quad (\text{A7})$$

where F_x is percentage (w/w) of liquid loading, δ_e the density of the liquid and a_1 the area per gram of the support.

From the rapid increase in adsorption in Fig. 4 in a loading range of *ca.* 5–7% it seems reasonable to conclude that an increase in the number of droplets rather than an increase in the drop size takes place when the loading is increased. The rapid increase in adsorption ceases at *ca.* 6% liquid loading. From this $h\bar{x}$ is estimated to correspond to a loading of 6%. Varying h between 0.5 and 0.8 gives values to \bar{x} corresponding to loadings of 7.4–11.3% according to eqn. A7.

A tentative calculation has been made of the decrease in liquid surface area from the maximum at $x = h\bar{x}$ to a value of x corresponding to 20% liquid loading. The position of the maximum depends on the value of x_0 . We have assumed that the formation of droplets starts at 0.5% liquid loading (see Fig. 4), which gives a value of x_0 between $0.04\bar{x}$ and $0.06\bar{x}$ for $0.5 < h < 0.8$. The decrease in liquid surface area with liquid loading for a stationary phase wetting the support has been calculated from the paper of Martin¹. We have assumed the same percentage decrease of liquid surface area with liquid loading for octadecane as for β, β' -thiodipropionitrile in this paper. Finally, we have assumed that the decrease in liquid surface area from $x = h\bar{x}$ to $x = \bar{x}$ corresponds to 50% of the value one would normally expect from the values of β, β' -thiodipropionitrile.

The quotient between the liquid surface area at the maximum point and at 20% liquid loading has been calculated for different values of h . A variation of h between 0.5 and 0.8 gives a variation of the quotient of *ca.* 2.4 to 4.2. The decrease in adsorption with liquid loading for ethyl methyl ketone and diisopropyl ether from the maximum value to the value at 20% loading gives quotients of 3.4 and 4.5 respectively (see Fig. 4). The average value of 3.95 corresponds to a value of h of *ca.* 0.75 if the variation of the contribution from adsorption with liquid loading for $x > h\bar{x}$ is due to changes in the area of the liquid surface. If one assumes that the formation of a liquid film starts when the distance between the centres of the droplets is on average equal to $a \cdot r$ where $a > 2$ is a parameter, it can be easily shown that:

$$h = (2/a)^2 \quad (\text{A8})$$

The average value of $h = 0.75$ above gives $a = 2.3$, which means that the formation of a liquid film starts when the droplets are rather close to each other. This is in accordance with the shape of the curves in Fig. 4 and an almost linear increase of the adsorption contribution to the retention volume of the solutes with liquid loading up to the maximum value.

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