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## MIXED RETENTION MECHANISMS IN GAS-LIQUID CHROMATOGRAPHY

### III. DETERMINATION OF THE GAS-LIQUID ADSORPTION COEFFICIENT FOR DIISOPROPYL ETHER ON *n*-OCTADECANE

J. Å. JÖNSSON\* and L. MATHIASSEN

*Department of Analytical Chemistry, University of Lund, P.O. Box 740, S-220 07 Lund (Sweden)*

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#### SUMMARY

The contribution of adsorption to the retention volume for diisopropyl ether was measured on columns with different loadings of *n*-octadecane coated on glass beads. A theoretical calculation of the magnitude of the adsorption on the glass surface, through the liquid, enables the adsorption coefficient at the gas-liquid interface,  $K_I$ , to be calculated.

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#### INTRODUCTION

In a recent study<sup>1</sup> of adsorption effects on gas-liquid chromatographic (GLC) columns with *n*-octadecane as the stationary phase, coated on a silanized diatomaceous support, it was found that the adsorption on the surface of the liquid phase plays an important role in the retention of some polar compounds. To interpret the results that study, a knowledge of the area of the gas-liquid interface is required. To calculate such areas, values of gas-liquid adsorption coefficients ( $K_I$ ) can be used, but they are not available in the literature.

Adsorption effects at gas-liquid interfaces have been reviewed by Martire<sup>2</sup> and more recently by Conder and Young<sup>3</sup>. There has been a debate about the existence of such adsorption, probably settled by Conder<sup>4</sup>.

In this work the GLC determination of  $K_I$  for diisopropyl ether on the surface on *n*-octadecane has been attempted. This system is one of those studied earlier<sup>1</sup>.

#### THEORETICAL

Retention in GLC is generally due to a combination of partition and adsorption, causing two separable<sup>5</sup> contributions to the total retention volume. At an infinitely small sample concentration, the adsorption contribution can be written<sup>6</sup> (see the list of symbols at the end of this paper):

$$V_N^A = K_I A_I + K_S A_S + K_A A_A \quad (1)$$

If we can assume that the liquid phase completely wets the support surface,  $A_A$  is zero. Further, if the liquid film is thin enough and if the surface is smooth, the areas  $A_I$  and  $A_S$  will be identical, so

$$V_N^A = (K_I + K_S)A \quad (2)$$

To approach the conditions that make eqn. 2 valid, we used unsilanized glass beads as the solid support. The surface area,  $A_I$ , of the liquid coated on the glass beads will be lower than the geometrical area of the beads, as the liquid will tend to accumulate at the points where the beads are in close contact with each other. This necessitates retention volume measurements at different liquid loadings and extrapolation to zero liquid loading.

According to eqn. 2, in order to determine  $K_I$  from experimental results for  $V_N^A$  and  $A$  we need an estimation of  $K_S$ . This constant is small and difficult to measure; therefore, a theoretical calculation is attempted.

By definition,  $K_S$  is given by

$$K_S = \frac{\Gamma_s}{C_g} \quad (3)$$

at infinite dilution where both  $\Gamma_s$  and  $C_g$  approach zero. Assuming that the gas phase is ideal, and that the solution of sample in the liquid phase follows Raoult's law, we can express  $K_S$  in terms of molar fractions of sample in the bulk liquid and in the surface layer at the support surface:

$$K_S = \frac{X_1^s}{X_1} \cdot \frac{RT}{a_1 p_1^0} \quad (4)$$

From Everett<sup>6</sup>, who systematized the thermodynamics of adsorption from solutions, we obtain an expression for  $X_1^s/X_1$  (when those molar fractions approach zero) giving

$$K_S = \frac{RT}{a_1 p_1^0} \cdot \exp\left[\frac{a_1(\sigma_2^0 - \sigma_1^0)}{RT}\right] \quad (5)$$

The quantities  $\sigma_1^0$  and  $\sigma_2^0$  are liquid–solid interface tensions between the pure liquids and the solid. Such interfacial tensions are difficult to measure, but Eon<sup>7</sup> has pointed out an interesting connection between relative interfacial tensions and the solvent strength parameters,  $\epsilon^0$ , introduced into liquid chromatography theory by Snyder<sup>8</sup>. The following relationship was given<sup>7</sup>:

$$\sigma_{\text{pentane}}^0 - \sigma_i^0 = 0.125 \epsilon_i^0 \quad (6)$$

Eqn. 6 is written for 60°C and for interfacial tensions expressed in SI units, so the numerical factor is different from that in ref. 7.

Values of  $\epsilon_i^0$  have been tabulated for different pairs of liquids and solvents<sup>8</sup>, which makes it possible to calculate an approximative value of  $K_S$  for diisopropyl ether adsorbed on glass from a solution in *n*-octadecane.

The molar area,  $a_1$ , of diisopropyl ether is estimated from data for critical temperature and pressure<sup>9</sup> by means of Hill's equation<sup>10</sup>; the result is  $2.6 \cdot 10^5 \text{ m}^2 \text{ mole}^{-1}$ . The vapour pressure,  $p_1^0$ , at 60°C of the same substance<sup>9</sup> is  $8.5 \cdot 10^4 \text{ Pa}$ . The solvent strength parameter,  $\epsilon_1^0$ , is taken from ref. 8 (Table 8-1 and eqn. 8-6a), giving  $\epsilon_1^0 = 0.22$  on silica, which has a surface structure similar to that of glass. For *n*-octadecane,  $\epsilon_2^0 = 0.05$  was used in the calculation. This value should be a low estimate, as  $\epsilon_{\text{pentane}}^0$  is 0.00 by definition and  $\epsilon_{\text{decane}}^0$  is 0.03 (ref. 8). If the real value of  $\epsilon_2^0$  is higher, it will result in a smaller value of  $K_S$ .

Inserting these values into eqns. 5 and 6 gives  $K_S = 0.9 \cdot 10^{-6} \text{ m}$ . Taking into account the uncertainties in the values given above, we estimate the true value of  $K_S$  to be between 0 and  $2 \cdot 10^{-6} \text{ m}$ .

It should be pointed out that we have assumed ideal solution behaviour of diisopropyl ether in *n*-octadecane. This was tested, considering the deviation of the infinite dilution activity coefficient,  $\gamma_1^\infty$ , from unity. The following equation<sup>11</sup> was used:

$$\gamma_1^\infty = \frac{RT\delta_2}{K_L p_1^0 M_2} \quad (7)$$

$K_L$  for the system under study was determined<sup>5,12</sup> to be 99.4. With the density for *n*-octadecane of  $\delta_2 = 0.7558 \text{ g cm}^{-3}$  (ref. 13), we find  $\gamma_1^\infty = 0.96$ , indicating a fairly ideal solution.

It should also be mentioned that we ignored any temperature dependence of the  $\epsilon^0$  values.

As will be seen later, the calculated value of  $K_S$  is small enough to be neglected in comparison with  $K_L$ , so slight errors in the calculation of  $K_S$  are of minor importance.

## EXPERIMENTAL

Glass beads (80–100 mesh; Alltech, Arlington Heights, IL, U.S.A.) were covered with 99% *n*-octadecane (Riedel de Haën, Hannover, G.F.R.) at different loadings between 0.05 and 1% (w/w). The coating was performed by dissolving the *n*-octadecane in *n*-pentane (p.a. grade; Merck, Darmstadt, G.F.R.), adding the glass beads and evaporating the solvent with gentle stirring. At normal room temperature the *n*-octadecane is solid, making the coated glass beads dry and easy to handle.

The surface areas of the glass beads were measured by the nitrogen thermal desorption method, first described by Nelsen and Eggertsen<sup>14</sup>. The value found was  $0.0134 \text{ m}^2 \text{ g}^{-1}$ , corresponding to a mean diameter of the beads of  $163 \mu\text{m}$  (the density was assumed to be  $2.5 \text{ g cm}^{-3}$ ), in good agreement with the sieve gradings (149–177  $\mu\text{m}$ ).

Glass columns (800 × 4 mm I.D.) were filled with the prepared packings.

All measurements were made with the apparatus described previously<sup>15</sup>. Diisopropyl ether (p.a. grade; Merck) was used as the sample. Dead volumes were measured with methane. Hydrogen was used as the carrier gas and the temperature was 60.0°C. Net retention volumes were measured at widely different sample concentrations and values of  $V_N^A$  were calculated using the procedure in ref. 5.

## RESULTS AND DISCUSSION

The experimentally measured values of  $V_N^A$  are presented in Fig. 1. A decrease in the  $V_N^A$  values with increasing liquid loading ( $\lambda'$ ) is seen. This should be extrapolated to  $\lambda' = 0$ . The fitting of a straight line to the data gives an intercept of  $0.73 \pm 0.17$  ml  $g^{-1}$  (95% confidence interval). If an exponential equation is fitted instead we obtain an intercept of  $0.76 \pm 0.16$  ml  $g^{-1}$ . Although the difference between these values is not significant, the value of  $0.76$  ml  $g^{-1}$  is considered to be more reliable. From eqn. 2 and the surface area of the glass beads ( $0.0134$  m $^2$   $g^{-1}$ ) we obtain  $K_1 + K_5 = (57 \pm 12) \cdot 10^{-6}$  m. From the estimation of  $K_5$  above we can calculate the rounded-off final result for  $K_1$  to be  $(55 \pm 15) \cdot 10^{-6}$  m. This value of  $K_1$  can be used to estimate the area of the gas-liquid interface for the columns in ref. 1.

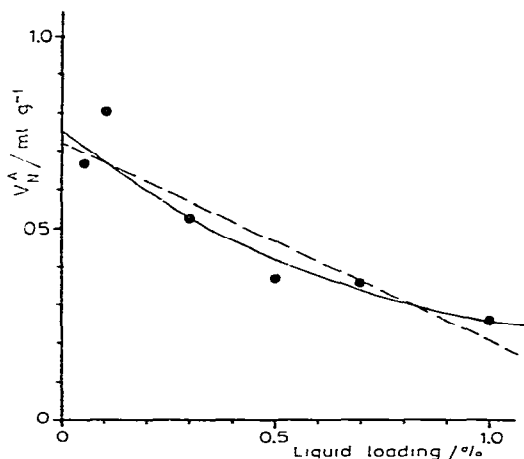


Fig. 1. Retention volume contribution from adsorption  $V_N^A$ , measured for diisopropyl ether on *n*-octadecane on glass beads at 60.0°C for various liquid loadings  $\lambda'$ .

The maximum value of  $V_N^A$  for diisopropyl ether on *n*-octadecane, which can be attributed to liquid surface adsorption, is *ca.* 15.5 ml per gram of packing. With our value of  $K_1$ , the area of the liquid surface at this maximum is calculated to be  $0.28$  m $^2$   $g^{-1}$ . This can be compared with the specific surface area of the support, which was measured as  $0.55$  m $^2$   $g^{-1}$  by the Nelsen and Eggertsen method<sup>14</sup>.

It is of interest to compare the  $K_1$  value with others obtained in similar systems of polar compounds on surfaces of non-polar liquids. Such literature data are rare. Pecsok and Gump<sup>16</sup>, however, have reported values evaluated from surface tension measurements. The general magnitude of these  $K_1$  values is much lower than our value of  $K_1$  for diisopropyl ether on *n*-octadecane. The discrepancy is due to the lack of measurements at low concentration. Inspecting Fig. 2 in ref. 16, one finds that the lines giving the  $K_1$  values can equally well be drawn with a considerably higher slope, giving values corresponding to the magnitude of our result. This supports the view expressed by Conder<sup>4</sup> that the gas-liquid interface adsorption is strongly dependent on concentration; it might be considerable with very small samples, but negligible with larger samples.

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## LIST OF SYMBOLS

$A$	Specific surface area of the support ( $\text{m}^2 \text{g}^{-1}$ )
$A_A$	Surface area of uncovered support (gas–solid interface area) ( $\text{m}^2 \text{g}^{-1}$ )
$A_I$	Surface area of the stationary liquid (gas–liquid interface area) ( $\text{m}^2 \text{g}^{-1}$ )
$A_S$	Surface area of support, covered with liquid (liquid–solid interface area) ( $\text{m}^2 \text{g}^{-1}$ )
$a_i$	Molar area of component $i$ ( $\text{m}^2 \text{mole}^{-1}$ )
$C_g$	Concentration in gas phase ( $\text{mol m}^{-3}$ )
$K_A$	Adsorption coefficient, gas–solid interface (m)
$K_I$	Adsorption coefficient, gas–liquid interface (m)
$K_L$	Partition coefficient, gas–bulk liquid
$K_S$	Adsorption coefficient liquid–solid interface (m)
$M_i$	Molecular weight of component $i$ ( $\text{g mole}^{-1}$ )
$p_i^0$	Saturated vapour pressure of component $i$ (Pa)
$R$	Gas constant ( $8.314 \text{ J}^\circ\text{K}^{-1} \text{ mole}^{-1}$ )
$T$	Temperature ( $^\circ\text{K}$ )
$V_N^A$	Contribution of adsorption to the net retention volume (ml)
$X_i$	Molar fraction of component $i$ , bulk liquid
$X_i^S$	Molar fraction of component $i$ , surface layer
$\Gamma_s$	Surface concentration ( $\text{mole m}^{-2}$ )
$\gamma_1^\infty$	Infinite dilution activity coefficient
$\delta_i$	Density of component $i$ ( $\text{g m}^{-3}$ )
$\varepsilon_i^0$	Solvent strength parameter, component $i$
$\lambda'$	Liquid loading (weight of liquid phase/weight of packing)
$\sigma_i^0$	Interfacial surface tension between component $i$ and solid support ( $\text{N m}^{-1}$ )

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