Adsorption Effects on Retention Behavior of Hydrocarbon Solutes in Gas Chromatography by Use of Polar Stationary Liquid Phase

Kunishige Naito, Shizuo Wada and Shinsuke Takei

Department of Industrial Chemistry, Faculty of Engineering, Ibaraki University, Hitachi 316

A mechanism of the solute retention in gas-liquid chromatography has been studied in the nonpolar hydrocarbon solute-polar stationary liquid phase system. N,N,N',N'-tetrakis(2-hydroxyethyl)ethylene diamine (THEED) was used as a polar stationary liquid phase. A dependence of the retention volume of the solutes and of the specific surface area of the liquid-coated, modified alumina upon the liquid loading was successfully interpreted on the basis of a previous model for distribution of the liquid phase on the modified alumina. The appearance of a maximum on the retention volume vs. liquid loading curve for the saturated hydrocarbon can be understood as a formation of the 1:1 solute-THEED adduct through the lateral interaction between the two molecules adsorbed on the modified alumina.

Keywords  Gas-liquid chromatography, retention mechanism, lateral effect, retention volume, N,N,N',N'-tetrakis-(2-hydroxyethyl)ethylene diamine

In gas–liquid chromatography, the bulk solution partition and/or some interfacial adsorption equilibria can concurrently contribute to the solute retention depending upon the nature of the solute, the type of the solid support and the polarity and the coated amount of the stationary liquid phase. In such a case, the retention volume, $V_R$, of a given solute is usually written as a linear combination of the above contributions:

$$V_R = K_L V_L + K_A A_L + K_S A_S$$

where $K_L$, $K_A$, and $K_S$ denote a distribution constant for partition into a bulk liquid phase layer (volume: $V_L$) and those for adsorption equilibria on the liquid layer (surface area: $A_L$) and on the solid surface (surface area: $A_S$), respectively. For a practical use of the above equation, it is necessary to establish a reasonable relationship between the interfacial area, $A_L$ and $A_S$, and the liquid loading on the basis of a possible distribution of the liquid phase on the solid support.

We previously found that experimental plots of the retention volume of the solute and the BET surface area of the liquid-coated, modified alumina against the liquid loading could be divided into five regions and into four parts, respectively, and that each part of the experimental plots could be fit with a straight line. From these results, we supposed that, as the liquid loading increased, the modified alumina surface, involving two subsurfaces with high and low adsorption capacities, was first covered with a monolayer, secondly with a double layer and finally with a bulk liquid layer of the stationary liquid phase. On the basis of this model, the specific surface area of the liquid-coated, modified alumina and the retention volume of the solute could be expressed as a linear function of the liquid loading in each region. Fitting these linear relations to the experimental plots, the distribution constants were calculated for the bulk solution partition and some interfacial adsorption equilibria.

In the present study, we attempt to interpret the mechanism of the solute retention in the hydrocarbon solute–polar stationary liquid phase [N,N,N',N'-tetrakis-(2-hydroxyethyl)ethylene diamine, THEED] system on the basis of the reasoning used previously. And the appearance of a maximum on the retention volume vs. liquid loading curve is discussed in terms of the lateral interaction between the solute and liquid phase molecules adsorbed on the modified alumina surface.

Experimental

Modified alumina, prepared from the active alumina Neobead MS-C (Mizusawa Industrial Chemicals, Tokyo, Japan) by a previous method, was used as a solid support. A commercially available solid support, Chromosorb P, was also used as a reference. After drying at 120°C for 4 h, 9 g of the modified alumina or 5 g of Chromosorb P was suspended in dichloromethane containing a desired amount of THEED (reagent for gas chromatography) and coated with THEED by evaporating the solvent. The liquid-coated support was packed into a stainless steel tube (100×0.3 cm i.d.) after removing any volatile component for 3 h.
under vacuum. The packed column was conditioned under the same conditions as those applied previously.

A Hitachi Model 063 gas chromatograph equipped with a thermal conductivity detector was used in conjunction with a Hitachi Model 056 recorder for gas chromatography. Chromatographic measurements were carried out at a column temperature of 60°C and with helium carrier gas at a flow rate of 40 cm³ min⁻¹. The same procedure as used previously was applied to the determination of the retention volume of each solute and its correction. Specific surface area of the liquid-free and liquid-coated, modified alumina was measured by the BET method nitrogen adsorption at liquid nitrogen temperature.

To prevent any fluctuations of the retention data with an alteration in an amount of the column packings used, a reduced retention volume, \( V_{N,R} \), was calculated by dividing the net retention volume by the weight of the liquid-free solid support packed into the column. And the liquid loading, \( X_L \), was taken as a weight ratio of the liquid phase to the solid support.

Results and Discussion

Figure 1A shows that the reduced retention volume for cyclohexene and 2-methylhexane increased with an increase in \( X_L \), linearly at a liquid loading higher than 6%. The linear increase in \( V_{N,R} \) with \( X_L \) suggests that the bulk solution partition is dominant for the solute retention in this case. For the solute with the same number of carbon atoms, the slope of the linear part of the \( V_{N,R} \) vs. \( X_L \) curve increases in the order: 2-methylpentane<hexane<1-hexene<2-hexene<cyclo-hexane<cyclohexene<benzene. A linear part of the \( V_{N,R} \) vs. \( X_L \) curve gives a positive intercept which is not in agreement with the \( V_{N,R} \) value at zero liquid loading. We could refer it to the effect of adsorption equilibrium at a gas–liquid interface. From the slope and intercept of the linear part of the \( V_{N,R} \) vs. \( X_L \) curve, the distribution constant for the bulk solution partition was calculated for each solute by correcting the effect of adsorption equilibrium at a gas–liquid interface on the solute retention (Table 2). These values are about one-third smaller than those obtained on the Triton X-100-coated Chromosorb P. Thus, the solutes have low solubilities in THEED under this condition.

In Fig. 1B, the \( V_{N,R} \) vs. \( X_L \) curves show different profiles from those of Fig. 1A. With increasing \( X_L \) up to 3%, \( V_{N,R} \) linearly decreased for cyclohexene, while that for 2-methylhexane increased to a maximum and then reduced. In this range of \( X_L \), the BET surface area of the THEED-coated, modified alumina was gradually decreased. A large decrease in \( V_{N,R} \) for an unsaturated hydrocarbon is not caused by a small reduction in the BET surface area but probably by deactivation of the modified alumina surface because active sites for adsorption are shielded with THEED molecules. At a liquid loading above 4%, \( V_{N,R} \) for either solute decreased gradually with an increase in \( X_L \). This gradual decrease, corresponding to a slow decrease in the BET surface area, was also observed for every solute other than benzene. In this liquid loading range, \( V_{N,R} \) of benzene increased linearly with \( X_L \). This result indicates the formation of the bulk liquid layer of THEED on the modified alumina, but the interfacial adsorption still plays an important role in the solute retention.

The parabolic curve of the \( V_{N,R} \) vs. \( X_L \) plot for a saturated hydrocarbon is in principle analogous to those observed on some types of graphitized carbon black coated with liquid phases. This phenomenon has been interpreted as an adsorption promoted through a lateral interaction between the solute and liquid phase molecules adsorbed on the solid surface. The previous authors considered that this phenomenon was observed only when chemically and geometrically homogeneous solid surface was partly covered with liquid phase molecules distributed in a monomolecular form. A planar surface of the graphitized carbon black can be regarded as one such homogeneous surfaces. But the metal oxide surface is in general considered to be a heterogeneous one because of the porous structure and because of the occurrence of some functional surface groups. In our previous studies, the experimental data were successfully interpreted by...
supposing that the modified alumina surface involved two subsurfaces with high and low adsorption capacities. It is likely that each subsurface is as homogeneous as the surface of the graphitized carbon black and that liquid phase molecules can be uniformly distributed on the subsurface in a monomolecular form. On the basis of this idea, the liquid phase molecules can interact with solute molecules even on the modified alumina surface through the lateral interaction. But we have observed the effect of the lateral interaction on the retention volume on the modified alumina.

In the paper of Di Corcia et al., a polar solute, such as a ketone or an alcohol, has a large maximum on the retention volume vs. liquid loading graph than a nonpolar hydrocarbon solute, when the graphitized carbon black was coated with Polyethylene glycol 1500. This result suggests that, on nonpolar surface of the graphitized carbon black, a molecule of the polar liquid phase can more easily interact with a molecule of the polar solute than with one of a nonpolar solute. On the modified alumina, a positively charged part as an active site for adsorption can strongly interact with an unsaturated hydrocarbon molecule. Since a polar molecule is fixed at the active site through this strong interaction, it appears that the polar molecule cannot interact well with the liquid phase molecule through the lateral interaction. However, a nonpolar solute molecule can interact more loosely with the active site and so more easily with the liquid phase molecule. Thus, on the modified alumina, only a nonpolar solute of a saturated hydrocarbon will give a maximum on the VN,R vs. XL curve.

Plots of VN,R against XL can be approximated with four straight lines for an unsaturated hydrocarbon and with one parabolic curve and three lines for a saturated one (Fig. 2). The XL values at an intersection of two adjacent curves, XL1, XL0 and XL0, are almost the same values for the solutes tested (Table 1). On the basis of the previous reasoning, the modified alumina surface involved two subsurfaces, subsurface 1 and subsurface 2, with high and low adsorption capacities. Supposing that subsurface 1 is preferentially coated with a monolayer of THEED and then subsurface 2 is covered, the XL1 corresponds to a liquid loading at which subsurface 1 is completely covered with a monolayer of THEED. Consequently, XL0 and XL0 are the liquid loadings where the modified alumina surface is completely covered with a THEED-monolayer and with a double layer of THEED, respectively.

In the lowest range of XL (region 1), the surface area of subsurface 1 covered with the THEED-monolayer (S1L) and that of the monolayer (S1M) are simply supposed to be proportional to XL as S1L=αXL and S1M=βXL, where α and β are proportionality constants. In this case, the BET surface area of the THEED-coated, modified alumina (S0) is written as a linear function of XL:

\[ S_0 = S_0^S - (\alpha - \beta)XL \] .......................... (1)

where S0 is the BET surface area of the liquid-free, modified alumina. Thus, adsorption equilibria on the uncoated part of subsurface 1, bare subsurface 2 and the monolayer of THEED can contribute to the solute retention. The VN,R vs. XL curve of hexane can be simply approximated as a parabola in this region. This approximation is valid for the curves of the other saturated hydrocarbons. We referred the effect of the lateral interaction to a formation of a weak 1:1 adduct of the saturated hydrocarbon with THEED. Thus, VN,R for the saturated hydrocarbon can be expressed as

\[ VN,R = K_1[1 + K_D(XL/S1)L](S1 - \alpha XL) + K_2S1 + K_3\beta XL \] .......................... (2)

where K1, K2 and K3 are the distribution constants for adsorption equilibria on the uncoated part of subsurface 1, bare subsurface 2 and the THEED-monolayer, K0 is the formation constant of the weak 1:1 adduct and S1 and S2 are the surface area of subsurface 1 and subsurface 2, respectively. The first
term of the right side of Eq. (2) corresponds to the contribution of the adsorption promoted on the bare subsurface 1 through the lateral interaction. Considering that \( K_S S^0_s = K_i S^1_t + K_2 S^2_t \), Eq. (2) can be written

\[
V_{N,R} = K_S S^0_s + (K_i K_0 - \alpha K_1 + \beta K_2) X_t - K_1 K_0 (\alpha / S_t) X_t^2
\]

\( ................................................ (3) \)

where \( K_S \) is an apparent distribution constant for adsorption on the modified alumina surface. \( V_{N,R} \) for the unsaturated hydrocarbon is given by neglecting the term containing \( K_D \).

\[
V_{N,R} = K_S S^0_s - (\alpha K_1 - \beta K_2) X_t ............................. (4)
\]

In region 2, the subsurface 2 is partly covered with the THEED-monolayer after the subsurface 1 has been completely covered. Supposing that the same values can be used for \( \alpha \) and \( \beta \), Eq. (1) is valid for this region. The same form of the equation as Eq. (5) in a previous paper\(^8\) can be derived by substituting \( V_{N,R}, S^0_s \) and \( X_t \) for \( V_N / W_a, S^0_a \) and \( W_t / W_a \).

In region 3, the modified alumina is considered to be covered completely with the monolayer and partly with the double layer of THEED. The surface area of the double layer and its occupied area are supposed to be simply proportional to the excess liquid loading, \( X_t - X_{10} \), necessary to form it. The BET surface area of the THEED-coated, modified alumina, in this case, can be expressed as the same form of the equation as Eq. (6) in a previous paper.\(^8\) Because of the high polarity of THEED, the double layer is considered to have as dense a structure as the monolayer, so that the solute molecule can get into the double layer only with difficulty. If we take account of the contributions of two interfacial adsorption equilibria on the monolayer and the double layer of THEED, the reduced retention volume of the solute can be written in the same form as Eq. (7) in a previous paper.\(^8\)

In region 4, the bulk liquid layer of THEED is formed on the modified alumina surface covered completely with the double layer of THEED. A decrease in \( V_{N,R} \) with increasing \( X_t \) suggests an important role of the interfacial adsorption and a less significant role of the bulk solution partition in the solute retention. Because of a low solubility of the solute in THEED, we did not consider the effect of adsorption at a liquid–solid interface on the solute retention. In this case, adsorption equilibria on the double layer and on the bulk liquid layer are thus mainly responsible for the solute retention. Considering that the surface area of the bulk liquid layer and its occupied area are proportional to the excess liquid loading, \( X_t - X_{10} \), to form the bulk liquid layer, the BET surface area of the THEED-coated, modified alumina and the reduced retention volume of the solute can be expressed as the same equation as Eqs. (8) and (9) in a previous paper.\(^8\)

These derived equations can be fitted to the experimental data of the retention volume and the BET surface area of the THEED-coated, modified alumina. The distribution constants for adsorption equilibria and for the bulk solution partition, and the formation constants of the 1:1 solute-THEED adduct are listed in Table 2 and Table 3, respectively.

### Table 2 Gas–liquid partition constants, \( K_i / \text{cm}^3 \text{ g}^{-1} \), of solutes in THEED

<table>
<thead>
<tr>
<th>Solutes</th>
<th>Chromosorb P</th>
<th>Modified alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylpentane</td>
<td>5.6</td>
<td>5.7</td>
</tr>
<tr>
<td>Hexane</td>
<td>7.6</td>
<td>7.8</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>16</td>
<td>21</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>9.6</td>
<td>10</td>
</tr>
<tr>
<td>2-Hexene</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>28</td>
<td>37</td>
</tr>
<tr>
<td>2-Methylhexane</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>Henepe</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>Benzene</td>
<td>72</td>
<td>105</td>
</tr>
<tr>
<td>1-Heptene</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>2-Heptene</td>
<td>21</td>
<td>25</td>
</tr>
</tbody>
</table>

\( K'_i \), for modified alumina, was calculated by supposing that \( K'_i = K'_2 \).

### Table 3 Distribution constants for adsorption, \( K_1, K_2, K_\alpha \) and \( K'_\alpha \), and formation constants of the 1:1 solute-THEED adduct, \( K_D \), on modified alumina

<table>
<thead>
<tr>
<th>Solute</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
<th>( K_\alpha )</th>
<th>( K'_\alpha )</th>
<th>( K_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylpentane</td>
<td>16.1</td>
<td>5.4</td>
<td>2.5</td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Hexane</td>
<td>22.4</td>
<td>7.1</td>
<td>2.8</td>
<td>3.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>13.0</td>
<td>6.5</td>
<td>2.8</td>
<td>2.8</td>
<td>2.9</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>77.8</td>
<td>7.9</td>
<td>2.8</td>
<td>3.1</td>
<td>3.2</td>
</tr>
<tr>
<td>2-Hexene</td>
<td>75.1</td>
<td>8.6</td>
<td>2.8</td>
<td>3.1</td>
<td>3.3</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>79.0</td>
<td>8.9</td>
<td>2.9</td>
<td>3.1</td>
<td>3.3</td>
</tr>
<tr>
<td>2-Methylhexane</td>
<td>61.2</td>
<td>16.9</td>
<td>4.1</td>
<td>6.5</td>
<td>5.7</td>
</tr>
<tr>
<td>Heptane</td>
<td>123</td>
<td>21.6</td>
<td>3.2</td>
<td>7.2</td>
<td>7.6</td>
</tr>
<tr>
<td>Benzene</td>
<td>—</td>
<td>21.6</td>
<td>—</td>
<td>4.1</td>
<td>4.4</td>
</tr>
<tr>
<td>1-Heptene</td>
<td>—</td>
<td>26.0</td>
<td>—</td>
<td>7.0</td>
<td>7.6</td>
</tr>
<tr>
<td>2-Heptene</td>
<td>—</td>
<td>26.2</td>
<td>—</td>
<td>7.7</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Unit: \( 10^9 \) cm for \( K_1, K_2, K_\alpha \) and \( K'_\alpha \), \( 10^4 \) cm\(^3\) for \( K_D \).
Tables 2 and 3. For the solutes other than cyclohexane, cyclohexene and benzene, the distribution constants for the bulk solution partition are estimated to have the same values independent of the type of the solid support used, as shown in Table 2. The reduced retention volume of these three solutes may involve the effect of adsorption at a liquid–solid interface, which can be neglected for chained hydrocarbon solutes, since they possess larger values for $K'_D$ than the others. As shown in Table 3, each solute gave the same values for $K_A$ and $K'_A$ though they were determined in different ranges of the liquid loading. This fact suggests that the surface characteristics of the double layer of THEED are very similar to that of the monolayer. That the values of $K_A$ and $K'_A$ for saturated and unsaturated hydrocarbons with the same number of carbon atoms and a similar molecular structure are almost the same indicates that the same type of interaction occurs probably through nonspecific interaction. For adsorption of hydrocarbons, the polar and heterogeneous surface properties of the modified alumina can be said to be generally converted to nonpolar and homogeneous ones by shielding with the thin film of THEED. The same result was obtained in a previous study using Triton X–100. It should be noted that the original surface properties of the solid are sufficiently shielded only with the monolayer. The liquid-coating method can be expected as an approach to convert the surface properties of the solid surface into the less active ones. Studies on this aspect are now in progress.

References


(Received October 1, 1987)
(Accepted November 26, 1987)