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INVESTIGATIONS OF THE RETENTION MECHANISM IN GAS-LIQUID PARTITION CHROMATOGRAPHY

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SUMMARY

A new graphical method is proposed for estimating the retention mechanism in gas-liquid partition chromatographic (GLPC) systems in which adsorption phenomena occur. The proposed method enables the adsorption phenomena accompanying the bulk liquid solution to be investigated unequivocally from gas chromatographic data alone. Moreover, it can be applied even in the very complicated instances of the GLPC systems with heterogeneous, and in addition not totally loaded, support surfaces. The utility of this method is demonstrated for two different GLPC systems with strong adsorption properties.

INTRODUCTION

One of the unresolved problems in gas-liquid partition chromatography (GLPC) is the influence of adsorption phenomena on the retention mechanism. In the early days of gas-liquid chromatography, adsorption effects were usually ignored, or at best considered to be insignificant. Pecsok *et al.*¹ and Martin², then Martire *et al.*^{3,4} and Pecsok and Gump⁵ first demonstrated the occurrence of gas-liquid interface adsorption in the overall retention mechanism. The important works of Scholz⁶, Fukuda⁷, Belenkij *et al.*⁸, Bieriezkin *et al.*⁹, Urone *et al.*¹⁰ and Parcher¹¹ have turned attention to the role of support surface adsorption.

While gas-liquid interface adsorption is a theoretically simple case of adsorption on a highly homogeneous liquid surface, support surface adsorption is a very complicated problem, for various important reasons.

Firstly, there may exist simultaneously areas of the support surface that are loaded with liquid phase and areas that are not covered with liquid, because of steric effects, surface tension of the liquid, etc. Also, the support surfaces are generally non-homogeneous, this heterogeneity being additionally modified by the presence of liquid in a very complicated manner.

The occurrence of adsorption phenomena in GLPC therefore introduces great complexity into the theoretical description of the overall retention mechanism. Typical analytical applications are also often complicated by the accompanying adsorption phenomena.

At the beginning of GLPC development, some efforts were made to eliminate

the adsorption effects by silanization¹²⁻¹⁷, alcohol modifications¹⁸ and in other ways. One of the simplest ways, although it is not always possible, is simply to increase the amount of liquid used, which decreases the relative contribution of the adsorption phenomena to the overall retention mechanism. However, it has been found that the simultaneous occurrence of bulk solution and adsorption often increases the column efficiency and the selectivity of separation¹⁹. The most promising approach therefore seems to be not the elimination of the accompanying adsorption phenomena, but their appropriate modification in different analytical situations. However, this approach can be used only when the retention mechanism, the mechanism of the adsorption phenomena in particular, is well understood. We shall further distinguish the three following retention mechanisms: bulk liquid solution, support surface adsorption, and gas-liquid interface adsorption.

The bulk liquid solution is simply a problem in the theory of liquid mixtures and it remains only to apply some results which have been obtained in the theory of liquid mixtures. It should be emphasized, however, that such an application is generally not easy, especially when the molecular theories of liquids are applied.

On the other hand, investigations of adsorption effects in GLPC are difficult, so that advances in this field (in the theoretical sense) are still needed. "For chromatography in which all three mechanisms occur, only the bulk liquid partition coefficient can be determined unequivocally by chromatography alone" wrote Conder *et al.*²⁰. More detailed investigations of the accompanying adsorption phenomena have so far been possible only by using other adsorption techniques, which led to the loss of the basic advantages of gas chromatography (speed and accuracy of measurements).

There still remains the problem of investigating these adsorption phenomena from gas chromatographic data alone. Recently, we have published three papers²¹⁻²³ that offer some possibilities in such investigations; they were developed on the basis of the temperature dependence of adsorption data.

The purpose of this paper is to present a new possibility of investigating these accompanying adsorption phenomena, based on the pressure dependence of adsorption data. The basic concepts underlying our new possibility have been taken from the theory of adsorption on heterogeneous surfaces.

THEORETICAL

The earliest concepts in the theoretical description of the retention mechanism in the presence of accompanying adsorption phenomena led to a three-term equation^{8,9,20}:

$$V_N = V_l K_l + V_s K_s + V_t K_t \quad (1)$$

where K_l , K_s and K_t are the partition coefficients for bulk liquid solution, support surface adsorption and liquid surface adsorption, respectively, and V_l , V_s and V_t are the volumes of the surface zones in which the above retention mechanisms occur. V_l is always identified with the volume of the liquid to be used in loading the support.

However, eqn. 1 has the obvious basic disadvantage that it assumes *a priori* that only three retention mechanisms (at most) exist in every chromatographic system. Of course, some new terms may be added in eqn. 1, but the theory of GLPC

developed so far does not provide any theoretical procedure for analyzing every term unequivocally.

In order to analyze the adsorption effects, we first separate the contribution $X_N(p, T)$ to the overall retention volume V_N , due to occurrence of the adsorption phenomena:

$$X_N(p, T) = V_N(p, T) - V_l K_l(p, T) \quad (2)$$

This is the well known procedure²⁴ of plotting V_N versus V_l at higher coverages of supports by liquids. p denotes the pressure of the solute in the free gas phase. The "adsorption retention", $X_N(p, T)$, corrected by the James–Martin compressibility factor, is simply equal to the adsorption isotherm derivative $\partial N_t / \partial \rho_0$, where N_t is the total amount of solute adsorbed on the support as well as on the liquid surface at a solute density of ρ_0 in the free gas phase.

Further, we shall use the concept of the area model of adsorbing surfaces²⁵, in which the whole adsorbent surface is assumed to consist of a number of areas each of which has identical adsorptive properties. The overall (total) adsorption isotherm, $N_t(p, T)$, is assumed to be the sum of the "local" isotherms, $N_i(p, T)$, that govern the local adsorption on appropriate areas of surface. The distinction between the adsorption areas is made on the basis of different adsorption energies, ε_i , characterizing the adsorption patches. Thus,

$$N_t(p, T) = \sum_{i=1}^r N_i(\varepsilon_i, p, T) \quad (3)$$

Our basic idea is to regard the liquid surface as an area of a hypothetical surface, being the sum of the areas where the support surface adsorption occurs and of the liquid surface.

Further, we shall assume that the adsorption on every area may in general be of a multilayer character. Moreover, we assume that the secondary (multilayer) adsorption on every area is also "specific", *i.e.*, it is characterized by parameters that are different for distinct patches. Then the eqn. 3 may be written in the form

$$N_i(p, T) = \sum_{t=1}^r [N_{ip}(\varepsilon_{ip}, p, T) + N_{is}(\varepsilon_{is}, p, T)] \quad (4)$$

where the subscripts p and s denote the primary and secondary characteristic local adsorptions, respectively.

Further assumptions will concern the model for the local primary and secondary adsorptions. Assuming the model of localized multilayer adsorption without lateral interactions, Hill²⁶ developed the following equation:

$$N_i(p, T) = \sum_{t=1}^r \sum_{x=p, s} N_{ix}^0 \left[1 + \frac{\alpha_{ix} \operatorname{sgn}(x)}{p} \exp\left(\frac{-\varepsilon_{ix}}{RT}\right) \right]^{-1} \quad (5)$$

where

$$\operatorname{sgn}(x) = \begin{cases} +1 & \text{for } x = p \\ -1 & \text{for } x = s \end{cases} \quad (6)$$

and

$$\alpha_{ix} = Q_{ix}^{-1} \exp\left(\frac{\mu_0}{RT}\right) \quad (7)$$

Q_{ix} being connected with the molecular partition function of one solute molecule, μ_0 the standard chemical potential and N_{ix}^0 the number of adsorption sites available for the ix th local characteristic adsorption.

In addition, we introduce the assumption of an ideally stepwise character of the overall adsorption process, which states that at every pressure, only one characteristic local adsorption occurs (either primary or secondary). In other words, at every pressure, eqn. 5 can be written in the form

$$N_i(p, T) = N_{ix}^{\Sigma} + N_{ix}^0 \left[1 + \frac{\alpha_{ix} \operatorname{sgn}(x)}{p} \exp\left(\frac{-\varepsilon_{ix}}{RT}\right) \right]^{-1} \quad (8)$$

where N_{ix}^{Σ} is the amount of solute adsorbed at the pressure at which the ix th characteristic local adsorption starts.

The errors introduced by the assumption of the ideally stepwise character of adsorption have recently been investigated theoretically by Harris^{27,28}, who pointed out that the lower the temperature, the more valid is the above approximation. Eqn. 8 can be written in the following differential form:

$$\frac{\partial \ln p}{\partial \ln N_i} = p \cdot \alpha_{ix} [\operatorname{sgn}(x)] \exp\left(\frac{-\varepsilon_{ix}}{RT}\right) + \varphi_{ix}(p) \quad (9)$$

where

$$\varphi_{ix}(p) = 1 + \frac{N_{ix}^{\Sigma}}{p} \cdot \frac{\partial p}{\partial N_i} \quad (10)$$

In the course of the first characteristic adsorption, $\varphi_{1p}(p) = 0$. Now, $\varphi(p)$ is a slowly varying function, as $\frac{\partial N_i}{\partial p} \cdot \frac{p}{N_{ix}^{\Sigma}}$ is simply the ratio of the actual derivative of the ad-

sorption isotherm to the tangent of the line joining the zero pressure point and the point where the ix th characteristic adsorption starts. As $\varphi(p)$ is a slowly varying function, it can be treated as a constant in a pressure interval corresponding to some characteristic local adsorptions.

Thus, the plot of $\partial \ln p / \partial \ln N_i$ against p should form a number of linear sections, of which the sections with positive slopes (tangent values) correspond to primary characteristic adsorptions, while those with negative slopes correspond to secondary characteristic adsorptions.

The Langmuir behaviour of the adsorbed phase, assumed by Hill²⁶ in developing eqn. 5, implies that the α_{ix} values may be identified with Henry's constants for appropriate characteristic local adsorptions. This enables us to calculate approximately the α_{ix} constants in a theoretical manner, as follows. From the theoretical considerations of De Boer²⁹ and Hobson³⁰, it follows that

$$\alpha_{ix} = 1.74 \cdot 10^4 \cdot (MT)^{\frac{1}{2}} \quad (11)$$

where p is the pressure (torr) and M is the molecular weight of the solute. Strictly, the α_{ix} values are different for distinct characteristic local adsorptions. However, the theoretical investigations of Hoory and Prausnitz³¹ showed that the adsorbent heterogeneity (*i.e.* the energy, ε_{ix}) has a small influence on Henry's constants, α_{ix} .

Thus, having α_{ix} , we can calculate ε_{ix} from the slope of the linear part in the

plot $\partial \ln p / \partial \ln N_i$ corresponding to the i xth characteristic adsorption. Further, the amount of solute molecules adsorbed in the pressure interval corresponding to some i xth characteristic adsorption is simply equal in this approximation to the number of adsorption sites available for this i xth characteristic adsorption. Thus, the plot $\partial \ln p / \partial \ln N_i$ provides all the information that is required in order to characterize a particular adsorption process.

In conclusion, the plot $\partial \ln p / \partial \ln N_i$ is a very simple method of analyzing unequivocally all the adsorption phenomena (characteristic adsorptions) that occur in a given adsorption (GLPC) system. One of its basic advantages is the fact that we do not have to assume *a priori* the kinds of characteristic adsorptions that occur in the adsorption (GLPC) system being investigated. The number of characteristic adsorptions (number of linear sections in the plot $\partial \ln p / \partial \ln N_i$) and their character (positive or negative slope) is a fully *a posteriori* result of the measurements and calculations made.

The main objection is the question of whether the model of localized adsorption is really appropriate for the gas-liquid interface adsorption. Fortunately, it has been found that the Langmuir equation is satisfactory also for adsorption systems with mobile adsorbed layers.

Now, returning to the "adsorption retention volume", $X_N(p, T)$, it is well known that in typical adsorption systems the solute in the free gas phase may, with good approximation, be considered to be an ideal phase. In this approximation, we obtain³²,

$$X_N(p, T) = RT \frac{\partial N_i}{\partial p} \quad (12)$$

Further,

$$N_i(p, T) = \frac{1}{RT} \int_0^p X_N(p, T) dp \quad (13)$$

From eqns. 12 and 13, it follows that

$$\frac{\partial \ln p}{\partial \ln N_i} = \frac{1}{p \cdot X_N} \int_0^p X_N(p, T) dp$$

Integration under the experimental curve $X_N(p)$ can be performed very easily and accurately, for instance by planimetry.

In conclusion, it can be seen from this theoretical section that the data required for investigating the retention mechanism in GLPC can be obtained solely by gas chromatography.

EXPERIMENTAL

In order to illustrate this graphical method for investigating retention mechanisms in GLPC, appropriate measurements and calculations have been performed for a number of GLPC systems, obtained by using Polsorb C loaded with mixtures of *n*-octadecanol and *n*-octadecane. Two types of GLPC systems were obtained. In the first type, the Polsorb C was loaded with different amounts (1, 2, 3, 5 and 10%, w/w) of a 1:1 mixture of *n*-octadecanol and *n*-octadecane. In the second type, the Polsorb C was loaded with 1, 2, 3, 5 and 10% (w/w) of a 3:1 mixture of *n*-octadecanol and *n*-octadecane, which enabled the bulk liquid partition coefficient, K_i , to be calculated.

It should be mentioned that Polsorb C is a support with strong adsorptive properties, its specific surface area being about $3.17 \text{ m}^2/\text{g}$ and its particle diameter $0.1\text{--}0.3 \text{ mm}$. Carbon tetrachloride was examined as the solute and its retention volume was measured at 85° , 95° and 105° . Different solute pressures in the chromatographic column were obtained by using different amounts of solute ($0.1\text{--}10 \mu\text{l}$), introduced by means of a Hamilton microsyringe. The measured retention volumes were related to peak maxima. Hydrogen was used as the carrier gas, cleaned by means of a type 5A molecular sieve. The flow-rate was about 50 ml/min . The chromatographic column was 2 m long and 4 mm I.D.

The experimental results presented in the next section concern the two GLPC systems that contained 5% (w/w) of liquid mixture.

RESULTS AND DISCUSSION

Before considering the experimental results, it should be emphasized that in developing eqn. 9 a number of simplifying assumptions were made. We ignored the significant lateral interactions in the adsorbed phase and the possibilities of lateral displacements. Later, we assumed a fully discrete distribution of adsorption energies and the fully stepwise character of the overall adsorption. The latter assumption is completely valid only in the zero pressure limit, and in the limit of infinite differences between the discrete energies of adsorption. Next, we ignored the pressure dependence of $\varphi(p)$, which is completely valid only in the case of completely linear overall adsorption isotherms.

It might therefore be expected that the accordance between the theoretical predictions from eqn. 9 and the experimental results would not be good.

Our purpose, however, was to investigate the adsorption mechanism in GLPC systems, *i.e.*, the sequence and the character of the local characteristic adsorptions. The quantitative information about the energetic conditions in a given GLPC system can be obtained by simply evaluating the adsorption isotherm $N_i(p, T)$ for this system from the derivative $X_N(p, T)$, and then analyzing this isotherm in the usual manner using the description of heterogeneous surfaces. We shall utilize such an analysis here, but we have evaluated the adsorption isotherms for our GLPC systems in order to obtain additional information, complementing the information obtained from the $\partial \ln p / \partial \ln N_i$ plots.

The calculated isotherms are presented in Fig. 1 (1:1 mixture) and Fig. 2 (3:1 mixture).

The most interesting feature in these plots is that they all have a local minimum at a solute pressure of about 0.015 atm . Such behaviour cannot be explained even by assuming a large energetic heterogeneity in a given GLPC or adsorption system. The only possible cause of this effect seems to be a large change in the behaviour of the liquid phase loading the support. We propose the following explanation for this effect.

Polsorb C is prepared from Carpathian diatomite earths, and therefore may be considered to a certain extent to be a support of the silica gel type. It is well known that in supports of the silica gel type, the alcohol molecules in the support-liquid interface are oriented in such a way that the alcohol hydroxyl groups lie outside the liquid surface. Consequently, the liquid surface tension should be similar to those of water, methanol and similar substances. Because of the strong induced polarization of

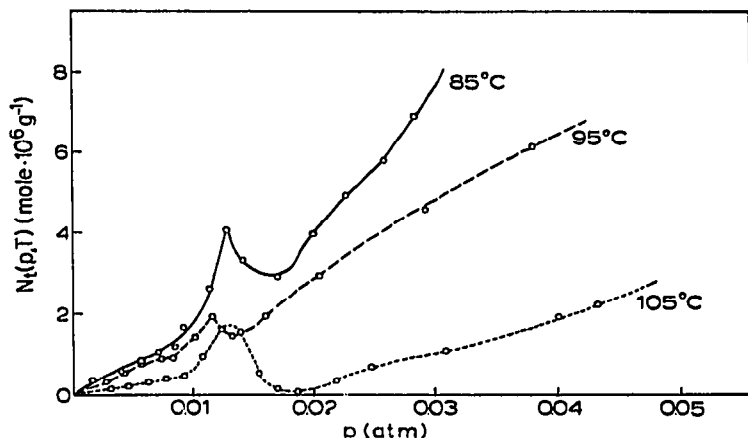


Fig. 1. Adsorption isotherms, $N_i(p, T)$, of carbon tetrachloride in the GLPC system containing 5% (w/w) of the 1:1 mixture, calculated from the retention volumes, $V_N(p, T)$, according to eqn. 2. The points on the curves denote the experimental pressures at which the functions $V_N(p, T)$ were measured. In order to show how reliable the calculations are, the values of $N_i(p, T)$ were also calculated for the same experimental pressures.

the carbon tetrachloride molecules, they interact strongly with the Polsorb C surface, and can therefore easily replace the alcohol molecules in the support-liquid interface zone, which should lead to a decrease in the liquid surface tension in the liquid-support interface zone. At a sufficiently low surface tension, the liquid phase enters the narrow pores, which so far were unavailable.

In the narrow pores are the most active adsorption centres³³, on which adsorption occurs at the lowest solute pressures (these are the first characteristic local adsorptions).

Because of the concurrent adsorption, the solute molecules adsorbed on these centres are removed, and it strongly decreases the amount of solute adsorbed. Further,

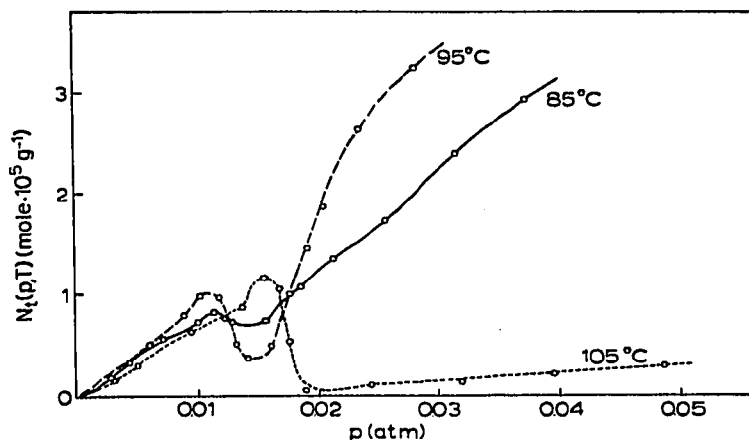


Fig. 2. Adsorption isotherms, $N_i(p, T)$, of carbon tetrachloride in the GLPC system containing 5% (w/w) of the 3:1 mixture.

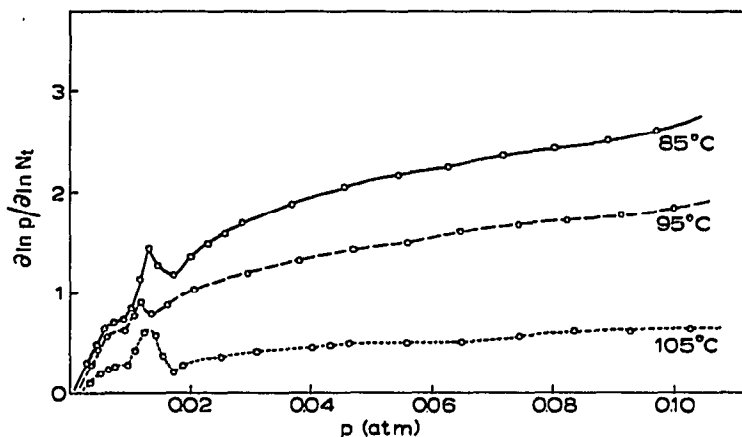


Fig. 3. Functions $\partial \ln p / \partial \ln N_t$ for carbon tetrachloride in the GLPC system containing 5% (w/w) of the 1:1 mixture, calculated from the isotherms $X_N(p, T)$ according to eqn. 14.

it might be expected that this effect would be stronger at higher temperatures, at which the surface tension becomes lower. This is, in fact, observed in our results. At the highest temperature investigated (105°), this effect leads initially to the total removal of the adsorbed solute. The latter adsorption is possible only on the liquid surface, or perhaps on a small part of the support surface in the very narrow pores that are still not yet covered by liquid phase.

Now, consider the $\partial \ln p / \partial \ln N_t$ plots for both of the investigated GLPC systems, shown in Fig. 3 (1:1 mixture) and Fig. 4 (3:1 mixture). Figs. 5 and 6 show the initial parts of the $\partial \ln p / \partial \ln N_t$ plots on a larger scale. The initial parts in Figs. 5 and 6 "analyze" the adsorption mechanism in the pressure interval from zero to the "penetration" pressure, at which the liquid phase enters the pores.

In the initial parts of the $\partial \ln p / \partial \ln N_t$ plots, two kinds of adsorption sites (two

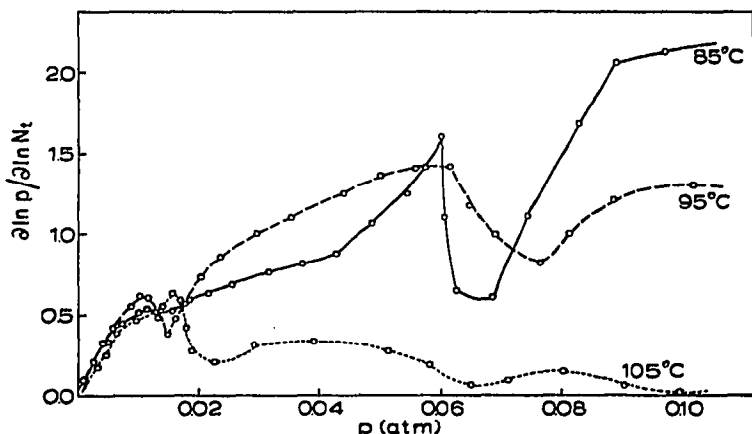


Fig. 4. Functions $\partial \ln p / \partial \ln N_t$ for carbon tetrachloride in the GLPC system containing 5% (w/w) of the 3:1 mixture.

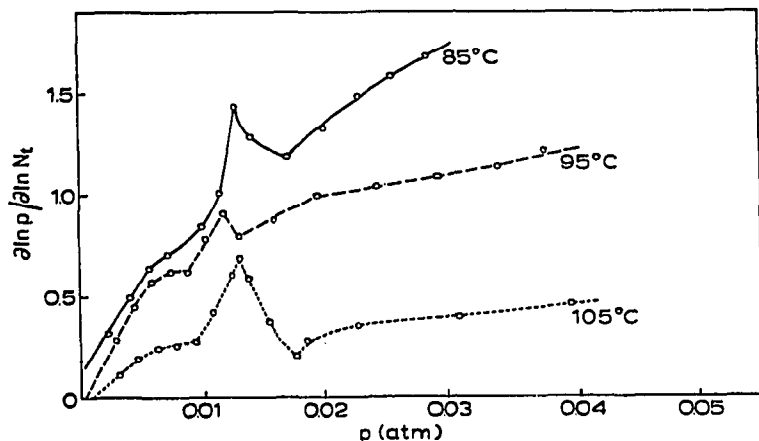


Fig. 5. The initial parts of the functions $\partial \ln p / \partial \ln N_t$, for the GLPC system containing 5% (w/w) of the 1:1 mixture.

characteristic local adsorptions) can be distinguished, corresponding to the two approximately linear sections with positive slopes.

An estimation of adsorption energies, made in Fig. 5 where the distinction is more clear, gives values of about 11,900 cal/mole for the first primary adsorption and 11,100 cal/mole for the second primary adsorption. These values were obtained at 75°, at which temperature, according to Harris's theoretical investigations^{27,28}, the estimation should be most reliable.

An estimation of the number of adsorption sites available for these primary adsorptions gives values of $1.13 \cdot 10^{-7}$ mole/g for the first primary adsorption and $4.08 \cdot 10^{-7}$ mole/g for the second primary adsorption. If we accept 6.1 Å as the slow-collision diameter of carbon tetrachloride molecules found by Lauger³⁴, then the support surface areas occupied by the first and second kinds of adsorption sites are 0.076 and 0.273 m²/g, respectively.

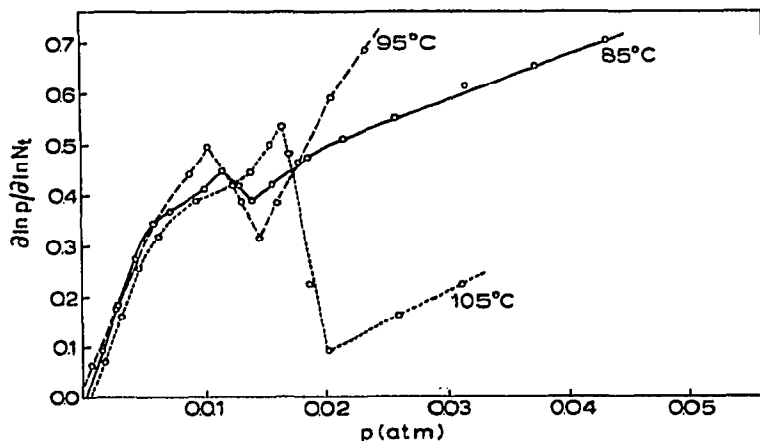


Fig. 6. The initial parts of the functions $\partial \ln p / \partial \ln N_t$, for the GLPC system containing 5% (w/w) of the 3:1 mixture.

A possible objection may be made as to whether the estimate of the number of adsorption sites is reliable if, for instance, the liquid mixture enters the pores before the formation of the solute monolayer on the second type of centres is completed. We do not consider that this occurs. The expected heat of solution, when identified with the energy of solution in the bulk phase, is much smaller than the value of 11,100 cal/mole found as the energy of adsorption on the second type of adsorption centres. According to the stepwise character of the overall sorption process in the surface phase, an effective solution does not take place until the complete monolayer is formed on the second type of adsorption centres. Thus, the "penetration" solute pressure cannot be reached until this monolayer has been completed.

Now, consider again Fig. 3. The last increasing section of the function $\partial \ln p / \partial \ln V_t$ probably represents the monolayer adsorption on the liquid surface and perhaps to some extent, it also shows the adsorption on some slightly adsorptive sites lying in the narrow pores, which are still not covered by liquid. Such a conclusion would be supported by Fig. 4, in which some linear sections above the "penetration" pressure can be observed. With the 3:1 mixture, the penetration of pores by liquid should be smaller than with the 1:1 mixture, owing simply to the fact that the replacement of alcohol molecules by carbon tetrachloride is, of course, lower at higher concentrations of alcohol in the loading mixture (here in the 3:1 mixture). It might be expected that the role of some characteristic adsorptions on slightly adsorptive sites at high solute pressures would be more significant in the GLPC system with the 3:1 mixture and, in fact, this is observed when comparing Figs. 3 and 4.

To summarize the information obtained in this work on the retention mechanism in the investigated GLPC systems:

(1) In the pressure interval from 0 to about 0.015 atm, the retention mechanism is predominantly connected with the physical adsorption of carbon tetrachloride on two highly adsorptive areas of support surface. This is a support-gas interface adsorption, as the highly energetic areas lie in narrow pores that are unavailable to the liquid phase because of the support-liquid interfacial tension.

(2) At about 0.015 atm, the formation of a monolayer on these highly energetic areas is completed, and then an effective bulk solution starts. Because of the decrease in the interface tension by carbon tetrachloride solved in bulk phase, the stationary phase enters the pores and removes the solute adsorbed previously on the highly energetic centres.

(3) At about 0.017 atm, this removal is completed, and then an effective adsorption starts on the liquid surface, which is now much greater than before because of the penetration of the pores by liquid. Simultaneously, some characteristic adsorption takes place on slightly adsorptive sites in the narrow pores which have still not been penetrated by liquid.

The pressure interval investigated was from 0 to about 0.1 atm. The retention mechanism was not investigated at higher solute pressures because, although higher solute pressures can be obtained by using sample sizes greater than 10 μl of solute, it is well known that, in the conventional elution chromatography, these larger sample sizes are not used and the retention mechanism at higher solute pressures is of no practical interest.

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